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Proceedings of the Natural Gas Research and Development Contractors Review Meeting

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Foreword

The Natural Gas Research and Development Contractors Review Meeting was held November 14 and 15, 1990, at the Lakeview Resort and Conference Center in Morgantown, West Virginia. This meeting was sponsored and hosted by the Morgantown Energy Technology Center of the U.S. Department of Energy (DOE).

The purpose of this meeting was to present results of the research in the DOE-sponsored Natural Gas Program, and simultaneously to provide a forum for real-time technology transfer, to the active research community, to the interested public, and to the natural gas industry, who are the primary users of this technology. The current research focus is to expand the base of near-term and mid-term economic gas resources through research activities in Eastern Tight Gas, Western Tight Gas, Secondary Gas Recovery (increased recovery of gas from mature fields); to enhance utilization, particularly of remote gas resources through research in Natural Gas to Liquids Conversion; and to develop additional, long term, potential gas resources through research in Gas Hydrates and Deep Gas. With the increased national emphasis on the use of natural gas, this forum has been expanded to include summaries of DOE-sponsored research in energy-related programs and perspectives on the importance of gas to future world energy.

Thirty-two papers and fourteen poster presentations were given in seven formal, and one informal, sessions:

- Three General Sessions (4 papers)
- Western Tight Gas (6 papers)
- Eastern Tight Gas (8 papers)
- Conventional/Speculative Resources (8 papers)
- Gas to Liquids (6 papers)

We gratefully acknowledge the participation of the American Gas Association, the DOE/Office of Fossil Energy, the DOE/Pittsburgh Energy Technology Center, and the Department of Defense/Naval Research Laboratory in the general sessions and in the poster session. The papers printed in these proceedings have been reproduced from camera-ready manuscripts provided by the authors. They have been neither refereed nor extensively edited.

Rodney D. Malone
Conference Coordinator

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Session 1

Unconventional Resources: Western Tight Gas

Western Gas Research

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ABSTRACT

The Western Gas subprogram is a multidisciplinary effort supporting the development of low-permeability, "tight" gas reservoirs in the western United States. The purpose is to determine the economic risks and technical feasibility of producing natural gas from tight formations. To realize this purpose, laboratory and field research is conducted, and industry is encouraged to develop the necessary understanding, technologies, and strategies. In order to accomplish this, two broad objectives have been defined for the Western Gas research program: (1) to reduce the uncertainty of reservoir production potential through an increased understanding of the resource, and (2) to improve extraction technology so that industry can assume development of the resource.

In pursuit of these objectives, the Western Gas research program consists of three technical elements -- geologic research, generic research, and production research -- and a program management function. The program management function is a DOE function of planning, execution, control, and technical integration of the subprogram. Each of the technical elements is described here:

- **Geologic Research** -- Activities in geologic research have been focused on the location and economic production of gas from low-permeability gas formations, which requires a detailed study of the geologic constraints. Such detailed, basin-wide definition guides the development of specifications for reservoir diagnostics, stimulation design, and eventual estimation of gas reserves. Geologic research also updates and improves the data base used in the analyses of the technology requirements. FY 91 work by the USGS is centered on the Uinta basin of Utah.

- **Generic Research** -- Current year supporting generic research is centered on fundamental geoscience research on natural fractures, sedimentology, and geomechanics related to tight gas sands. METC modeling-based research is focused on the analysis of gas production systems in low-permeability gas reservoirs. Research in the METC in-house geoscience area is centered on fractured, tight gas reservoir technology. A new start in FY 91 will provide reserve estimates of commercially recoverable gas for the DOE priority basins, beginning with the Greater Green River Basin of Wyoming, Colorado, and Utah. The reserve estimates will be based on the USGS resource assessments already compiled for the priority basins.

- **Production Research** -- Activities in production research develop, test, and verify technology and techniques to improve recovery of gas from tight gas reservoirs. These

activities substantiate and verify results obtained from laboratory and modeling studies and increase the reliability of forecasts of recovery efficiency and extraction technology.

In FY 91, field research includes production verification and extraction efficiency testing in wells of opportunity. The purpose is to extrapolate technology developed at the multi-well experiment (MWX) site and to evaluate reservoir properties and production performance across the Piceance basin through well tests, geologic analysis, and core and stimulation testing.

The major field activity of FY 90 was the drilling of the slant well in western Colorado. During drilling and coring of the well, a number of promising indicators of great production potential were observed, such as large gas kicks against 16 to 16.5 pounds per gallon drilling mud and the discovery of open natural fractures in high angle and horizontal cores. However, due to severe, unforseen drilling and completion problems, the well had to be temporarily abandoned after a string of drill pipe had become firmly cemented in the well. About 5,300 feet of the fish were recovered before lack of further progress and depletion of funds forced a stop to the work.

An option to sidetrack and redrill the slant hole is currently being considered. The well could be reentered, and about 5,300 feet of the 7-inch casing (uncemented to the top of the fish) could be pulled out of the well. This would permit sidetracking around the lost part of the hole to redrill the 60-degree and horizontal hole sections. In view of the large volumes of drilling mud lost to the formation and the resulting formation damage, the new hole would be about 1,000 feet to one side of the original well in the target zones. These targets consist of the horizontal leg in the Upper Cozzette blanket sand and the 60-degree slant hole through the interbedded channel sands and coal seams of the paludal interval.

Preliminary Report on the Characterization of Tertiary and Cretaceous Low-Permeability (Tight) Gas-Bearing Rocks in the Uinta Basin, Utah

CONTRACT INFORMATION

Contract Number	AI21-83MC20422-1 MOD A041/A043	
Contractor	United States Geological Survey Branch of Petroleum Geology MS 934, Denver Federal Center Lakewood, Colorado 80225-0046	
Contactor Project Manager	Thomas D. Fouch	
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Period of Performance	October 1, 1989 to September 30, 1990	

INTRODUCTION

Gas-bearing low-permeability (tight) sandstone reservoirs in the Uinta Basin occur primarily in the north-central and eastern parts of the basin, although Cretaceous rocks are largely untested over much of the northern and western parts of the basin (Figure 1). Spencer and Wilson (1988) suggest that much of the Cretaceous section in the undrilled areas will be prospective for gas in tight reservoirs of the Mesaverde Group. However, although some new information on the Cretaceous sequence in the western and northern areas of the basin is presented in this paper, interpretations of the occurrence and character of gas reservoirs in these strata are very speculative.

Gas-bearing sandstone reservoirs in the basin that commonly contain porosity values ranging from 8 to 16 percent, but whose matrix permeabilty values are 0.1 md or less are frequently termed "tight gas" sandstones. Most reservoirs are lenticular fluvial sandstones that occur within two major sedimentary systems (Figure 2).

In the first sedimentary system, Upper Cretaceous impermeable fluvial rock reservoirs occur within the Tuscher, Farrer, Neslen, Blackhawk, Sego, Castlegate, and Price River Formations which are assigned to the Mesaverde Group. A second sedimentary system consists of Tertiary rocks that occur in the Paleocene and Eocene Wasatch and Colton Formations, and the Maastrichtian to early Eocene North Horn Formation. Locally, fluvial sandstones of the Paleocene to Eocene Green River Formation are tight-gas reservoirs but many operators frequently group the fluvial Green River reservoirs with those of the Wasatch Formation.

U.S. Geological Survey studies of oil- and gas-bearing Upper Cretaceous and lower Tertiary strata in the basin are designed to characterize the reservoir units, and to assess the gas resources in the basin's tight siliciclastic reservoirs. The U.S. Department of Energy's Western Tight Gas Sands Program is a major funder of this endeavor as are the U.S. Geological Survey's Onshore Oil and Gas, and Evolution of Sedimentary Basins Programs. This preliminary report indicates the nature and progress of some studies we are pursuing in support of the characterization and assessment effort. The report presents figures that incorporate new information and interpretations. However, these figures are preliminary and improved versions and a more complete treatment of the topic are intended to appear in subsequent reports. Figure 2 is a cross section that extends from overpressured tight sandstone and carbonate reservoirs at Altamont oil and gas field in the north-central part of the basin to the region of gas production from normally pressured to slightly overpressured Tertiary and Cretaceous strata which lies east of the Green River. The

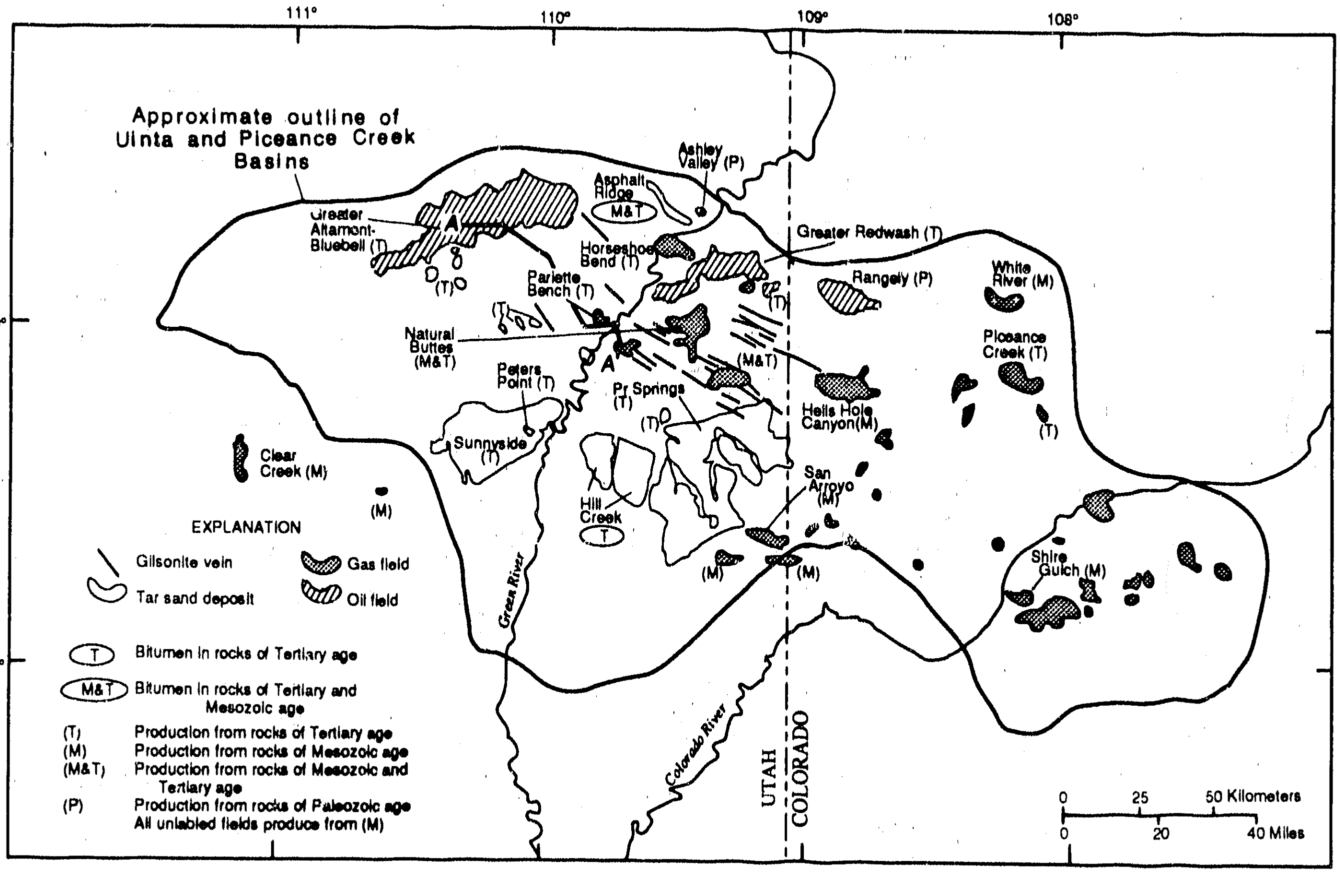

Figure 1. Index map of the Uinta and Piceance basins showing area of principal hydrocarbon accumulations and line of section A-A' for cross section of figure 2.

vast majority of successful tight-gas completions have been in Tertiary strata. Successful completions in Cretaceous rocks are few and data sufficient for analysis of Cretaceous units are likewise sparse. A number of companies are currently very active in Wasatch gas exploration. Some are attempting to complete in Cretaceous Mesaverde gas-bearing rocks where they underlie the productive Tertiary units and where gas from each formation can be commingled.

ELEMENTS FOR CHARACTERIZATION AND ASSESSMENT

Stratigraphy and Structure of Gas-Bearing Strata

Figure 3 is a map that shows major faults and gilsonite veins in fractures in the Uinta Basin. Information on the structural composition of the basin was derived primarily from Cashion (1973), Campbell (1976), Ryder and others (1976), Fouch (1975), Rowley and others (1985), and Bryant (in press). Much of the gas production is from fields developed along the trace of faults and fractures in the eastern part of the basin. The trend of the gilsonite veins and several of the fault zones in the southern and eastern parts of the basin appear to overlie and coincide with the position of the Douglas Creek, Seep Ridge, and Gar Mesa faults of Stone (1977). We suggest that the structural discontinuities that cut the Tertiary and Cretaceous units of the basin represent reactivation of covered structures associated with the ancestral Uncomphagre uplift. We believe that gas has migrated from Cretaceous source rocks through a permeable network of faults and fractures in Cretaceous and Tertiary strata to the slightly overpressurred to normally pressured reservoirs of the Mesaverde Group and Wasatch Formation in the eastern part of the basin.

Stratigraphic identifications used in making maps and sections are based on comparison of the wireline-log character (signature) to that of published identifications

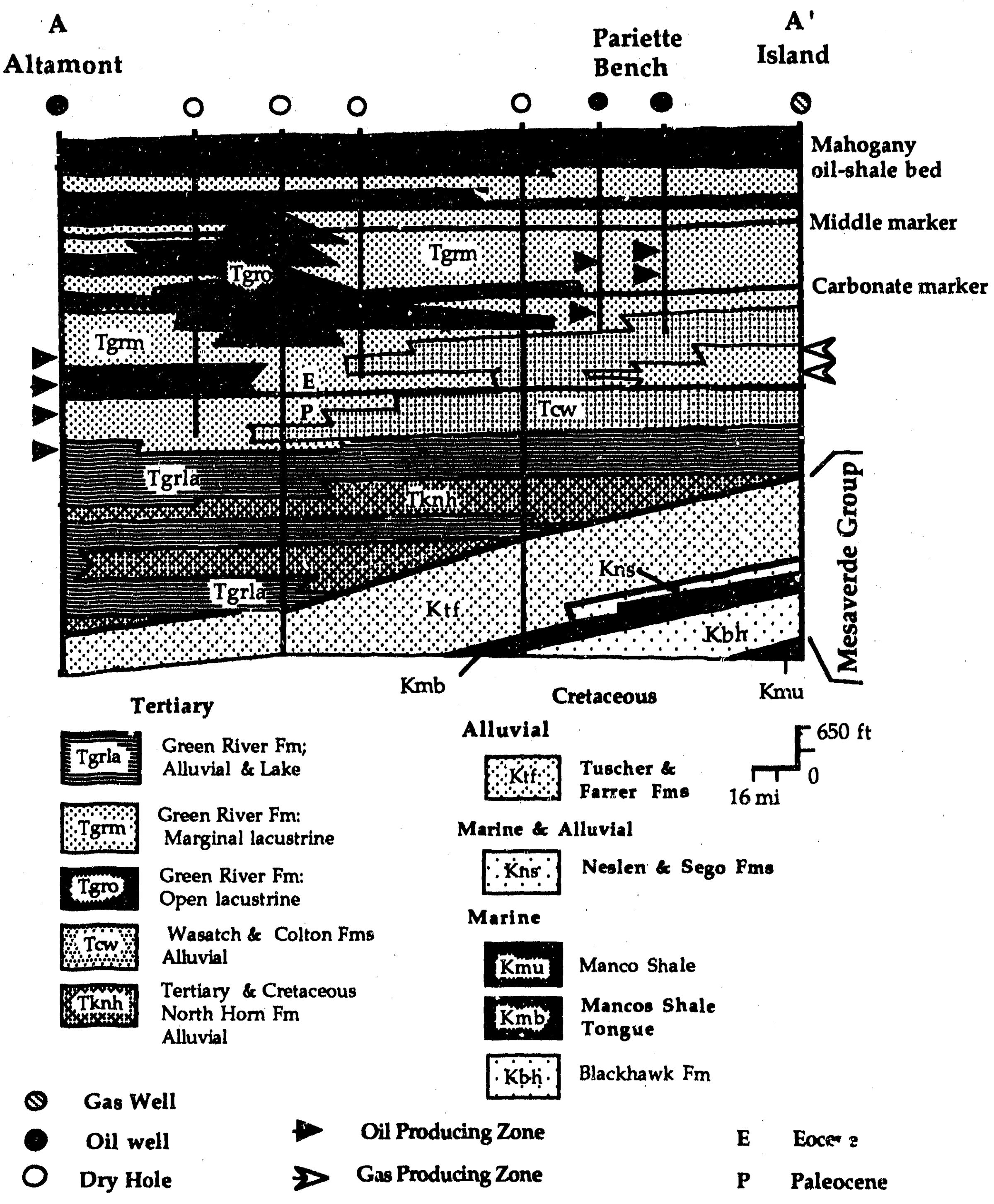

Figure 2. Stratigraphic cross section A-A' that extends from the Altamont oil and gas field in the north-central part of the basin to the Island gas field (modified from Pitman and others, 1982). Section illustrates productive sedimentary systems. Beds in Island field are typical of those of the basin's region of gas production from the so-called tight Tertiary and Cretaceous strata which lies east of the Green River. See figure 1 for line of section.

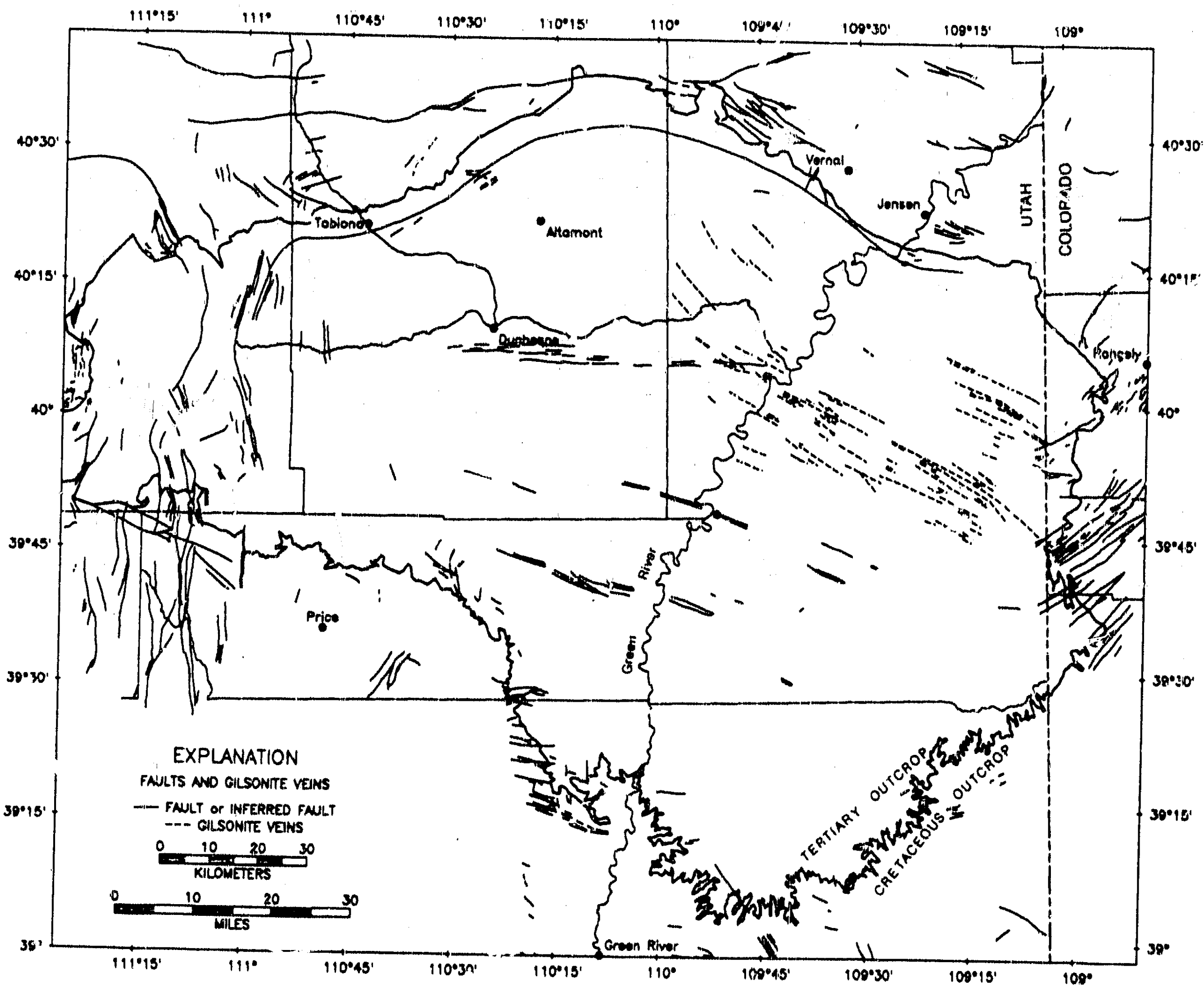

Figure 3. Preliminary map showing gilsonite veins (dashed lines) and faults (solid heavy lines) in Tertiary and Cretaceous rock. Faults are taken from Cashion (1973); Bryant (in press); Campbell (1976); R.W. Scott, R.C. Johnson, and M.P. Pantea, personal commun.(1990); and L.F. Hintze (1980).

(character of tops and markers), and to other surface and subsurface lithologic characteristics unique to individual formations. The stratigraphic data base includes more than 1,500 identifications by us and more than 23,000 from other sources. This stratigraphic subdivision serves as a frame of reference for quantifying the number of reservoir sandstone units, their porosity and permeability values, and their geometries. The subdivision has been used to construct several maps for use in the assessment of gas resources. These maps help to characterize and quantify that part of the stratigraphic section that either is known to be, or may be, gas-bearing.

Figure 4 is a structure contour map of the top of the Upper Cretaceous Mesaverde Group. The westernmost part of the basin has been excluded from the map area because it contains allochthons of the thrust belt. The sequence of reservoirs contained within the Mesaverde section is anticipated to contain the principal Cretaceous gas-bearing unit in much of the basin. Figure 5 maps the base of that part of the Upper Cretaceous Mesaverde section that we are considering in this study. The map was constructed from interpretations of the base of the Blackhawk or Star Point Formations of the Mesaverde Group, or the top of the Mancos Shale. These markers represent a westward-downstepping set where each marker is progressively older. Figure 6 is an isopach map of the potential reservoir section of the Mesaverde Group.

Thermal History

The thermal maturity of the Mesaverde Group is being determined by vitrinite reflectance on samples from drill holes and by coal rank data. Samples of the

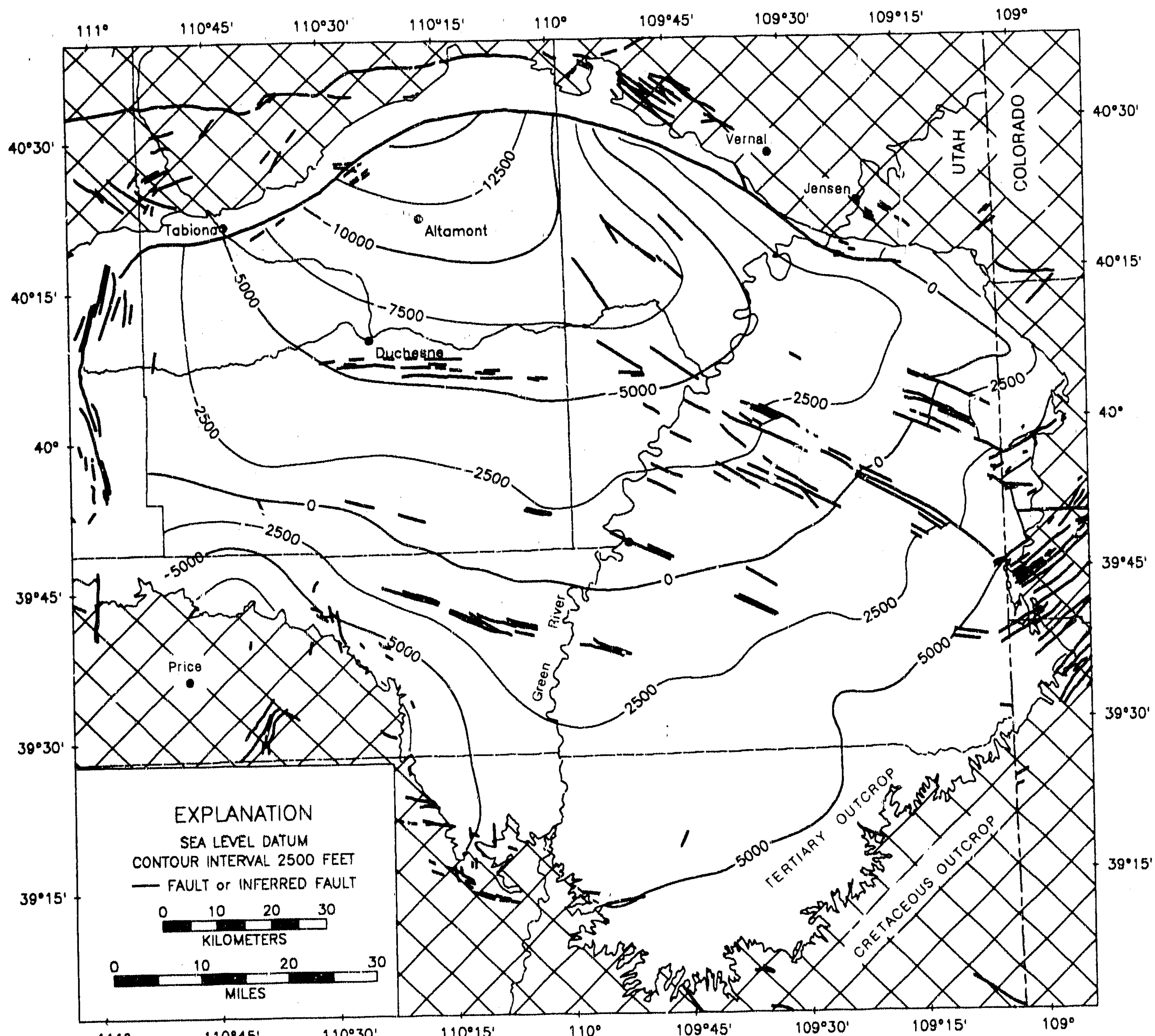

Figure 4. Preliminary structure contour map of the top of the Cretaceous strata. The westernmost part of the basin has been excluded from the map area where it intersects allochthons of thrusted strata.

Wasatch and Green River Formations and the Eocene Uinta Formation are being analyzed for vitrinite reflectance and by Rock-Eval pyrolysis. The surface and near-surface data when plotted with the data from the Mesaverde allow construction of vertical maturation profiles. These maturation profiles enable us to (1) approximate the magnitude of past temperatures, (2) estimate amounts of erosion, (3) estimate timing of oil/gas generation, and (4) taken with porosity measurements, infer the amount of porosity in strata of the basin yet to be penetrated. As a result, these data will be used in our assessment of the Uinta Basin's tight gas resources.

Two regional vitrinite reflectance (Rm) maps are being constructed for the Uinta basin; one showing the elevation of the 0.73% vitrinite-reflectance level, and the other the elevation of the 1.10% level (see Nuccio and Johnson, 1989). The 0.73% Rm level was chosen because it represents the level of maturity needed for the onset of gas generation from humic type III organic matter, the principal type of organic matter that we have identified in the nonmarine sedimentary rocks of the Upper Cretaceous tight-gas section. The 1.10% Rm level was chosen because it represents peak methane generation for type III kerogen.

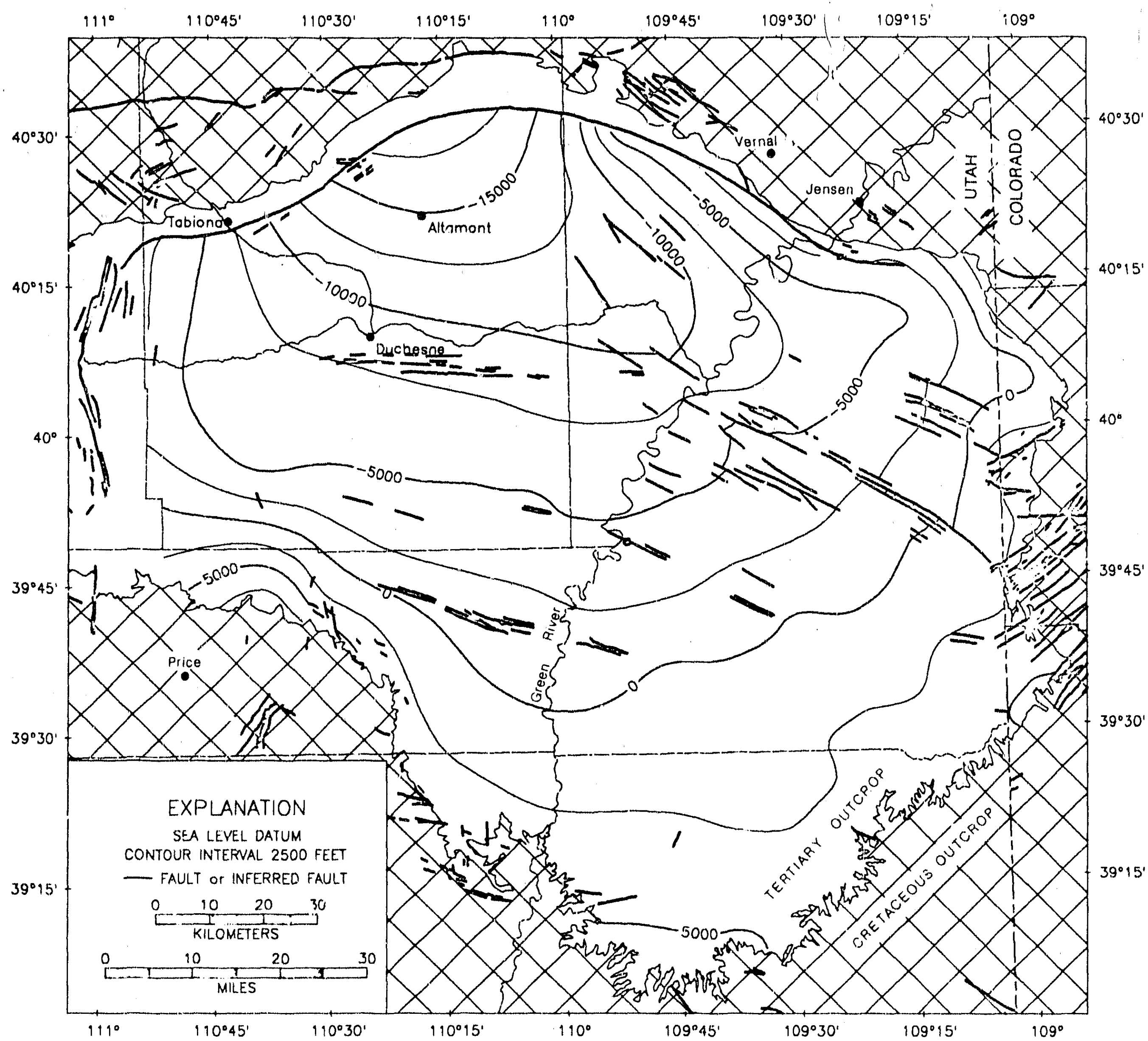

Figure 5. Preliminary contour map of the base of the Upper Cretaceous Mesaverde section that we are considering in this study. The sequence of reservoirs within the Mesaverde section is anticipated to contain the principal Cretaceous gas-bearing units in much of the basin.

Natural Gases

Two types of thermochemical natural gas can be distinguished in the Uinta Basin based on chemical and carbon isotope composition. One type is chemically dry and isotopically heavy and was generated from type III (nonmarine-woody) kerogen at advanced stages of thermal maturity. This nonassociated gas occurs in Mesaverde and Wasatch reservoirs at depths as great as 9,300 ft in the Red Wash and Natural Buttes fields. The Wasatch gases occur in reservoirs that are marginally mature in reference to hydrocarbon generation, yet are almost identical in composition to gases of the underlying Mesaverde Group. Gases in the Wasatch are interpreted to have migrated vertically from deeper, more mature source rocks with type III kerogen in the Mesaverde.

The discovery that some of the Wasatch gas is generated in underlying Cretaceous rocks has encouraged some companies to attempt Upper Cretaceous Mesaverde tests in those regions where Wasatch reservoirs are gas-bearing. A number of companies are

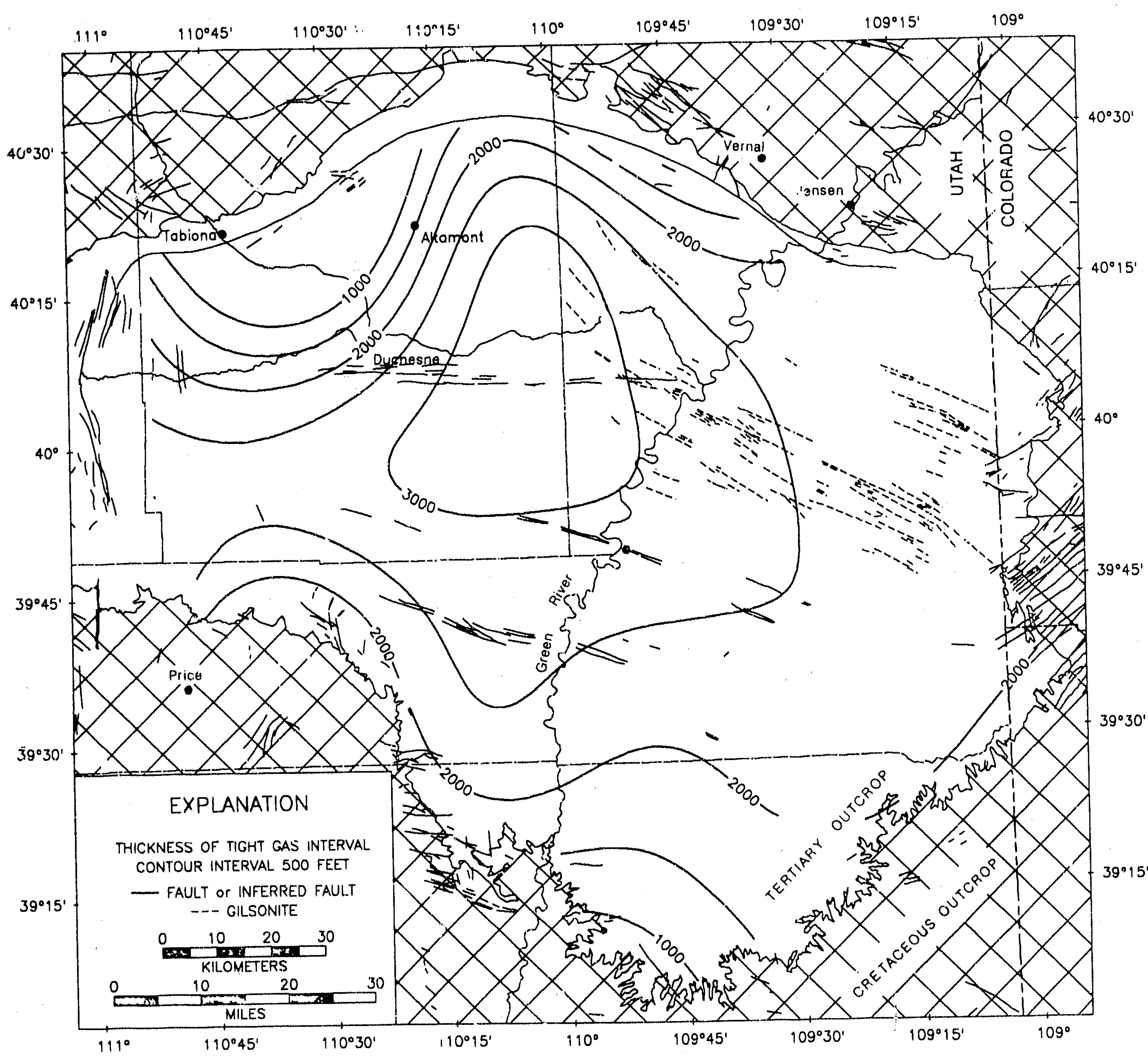

Figure 6. Preliminary isopach map of the Mesaverde Group. The map excludes the westernmost part of the basin where thrusted allochthonous Cretaceous rocks are preserved, and it excludes Cretaceous and older beds north of the subsurface basin-boundary fault. Map shows thickness and extent of section that contains potential impermeable gas reservoir units.

currently attempting to penetrate and complete in Cretaceous Mesaverde gas-bearing rocks where they underlie the productive Tertiary units.

In contrast, the second type of gas is chemically wet and isotopically light. It was generated at intermediate stages of thermal maturity from type I (lacustrine) kerogen associated with the sediments deposited in ancient Lake Uinta. These wet gases are associated with oil and are restricted to Eocene and Paleocene reservoirs in the Green River Formation and bounding beds of the Wasatch, North Horn, Colton, and Uinta Formations in the north-central and northeast parts of the basin.

Reservoir Characterization

In Tertiary strata, principal oil and gas reservoir rocks are diagenetically altered fluvial channel, deltaic, and open lacustrine sandstones, including turbidites in Altamont. These reservoirs formed near the margin of ancient Lake Uinta. The channel-form bodies in petroliferous surface exposures of the basin's south flank can be separated into two distinct types with respect to geometry and width/depth (W/D) ratio. "Type one" is characterized by a tabular geometry controlled by a planar lower bounding surface, an average channel depth of 25 ft , and an average W/D ratio of 8.9. The planar channel bottom results from underlying resistant carbonate units whose early lithification restricted downcutting and caused more extensive lateral channel migration compared to that of streams forming "type two" bodies. Type two bodies are characterized by a lenticular geometry, by an average channel depth of 18.7 ft, an average W/D ratio of 3.6, and a concave-upward lower bounding surface. The absence of resistant carbonate rocks underlying streams that deposited type two bodies resulted in streams that, although similar in size, did not migrate laterally as much as those of type one and therefore established smaller sandstone bodies. The size of individual marginal-lacustrine channel sandstone bodies (and therefore reservoir units) is largely dependent upon induration of the substrate across which streams flowed.

Tertiary sandstone reservoirs at four localities in the Uinta Basin have been analyzed using petrographic and geochemical techniques in order to characterize their origins and reservoir properties. Sandstones from each of the four localities represent a different type of hydrocarbon reservoir based on porosity and permeability trends that reflect a distinct diagenetic and burial history. Preliminary analyses indicate that porosity enhancement or reduction and the levels of matrix permeability are controlled by burial-influenced diagenetic reactions related to original framework mineralogy.

Study of Tertiary fluvial gas-bearing strata of Natural Buttes field in the eastern part of the basin (Figure 1), indicates that moderately-buried, low-permeability feldspathic litharenites were diagenetically altered by both iron-bearing and non-iron-bearing carbonate, anhydrite and barite, and illite, illite/smectite, and kaolinite. Partial to complete dissolution of carbonate minerals is common in many rocks and enhances porosity, but widespread authigenic clay in secondary pores results in overall low permeability. Temporally equivalent and younger Tertiary lacustrine and fluvial strata at Pariette Bench field (Fig. 1) in the central part of the basin display mineralogic compositions and diagenetic and burial histories similar to Natural Buttes strata. However, bitumen in dissolution voids in Pariette Bench reservoirs indicates that petroleum migrated through these probably thermally-immature, partially overpressurred rocks late in their burial history.

In the northern and eastern parts of the Uinta Basin fluvial and lacustrine quartzarenites and litharenites generally are devoid of feldspar reflecting nearby sediment sources. In contrast, temporally and depositionally equivalent Natural Buttes and Pariette Bench sandstones contain abundant feldspar. These latter units were formed in streams entering the basin from southerly directions. At Bluebell-Altamont field in the north-central part of the basin, deeply-buried oil-stained sandstone units display low porosity (generally less than 8 %) and matrix permeability values (generally less than 0.1 md) caused by mechanical compaction and postdepositional mineral alteration. Numerous partially-mineralized, oil-stained and open natural fractures provide formation permeability in these otherwise low-permeablity strata.

Shallow-buried, thermally-immature fluvial and lacustrine quartzarenites and litharenites in the eastern part of the basin at Red Wash field show good matrix porosity and permeability values. Most intergranular pores show no evidence of early-formed mineral cements; this suggests primary porosity.

The fluvial and marine Upper Cretaceous Castlegate Sandstone is composed of a quartzarenite, more than 90 percent igneous, monocrystalline quartz grains and minor carbonate grains. The mineralogic suite contrasts with those in the underlying Blackhawk Formation and overlying Price River Formation, both of which contain more abundant sedimentary rock fragments, minor feldspar, and rare volcanic grains.

Figure 7 is a plot of core-plug porosity from 14 wells for nonmarine sandstones of the Mesaverde Group. The 25th to 75th porosity percentiles shown define an envelope that represents the middle one-half of the measured porosity range. Porosity is plotted against vitrinite reflectance (Rm) rather than depth to eliminate the effect upon the data of local topographic relief and of regional differences in uplift and erosion. In addition, porosity change can be linked to hydrocarbon generation by characterizing porosity in terms of Rm.

In an overall sense, the porosity of nonmarine sandstones of the Mesaverde Group is not low if the level of time-temperature exposure (Rm) is taken into account (Figure 7). Rather, as shown by the dashed trend lines superimposed upon the data of Figure 7, porosities are typical of sandstones in general. The unusual aspect of nonmarine Mesaverde sandstones is that porosities remain approximately constant as Rm increases from 0.7% to 1.8%. The porosity of most sandstones decreases as a power function of increasing Rm over this thermal-maturity range (Schmoker and Hester, 1990).

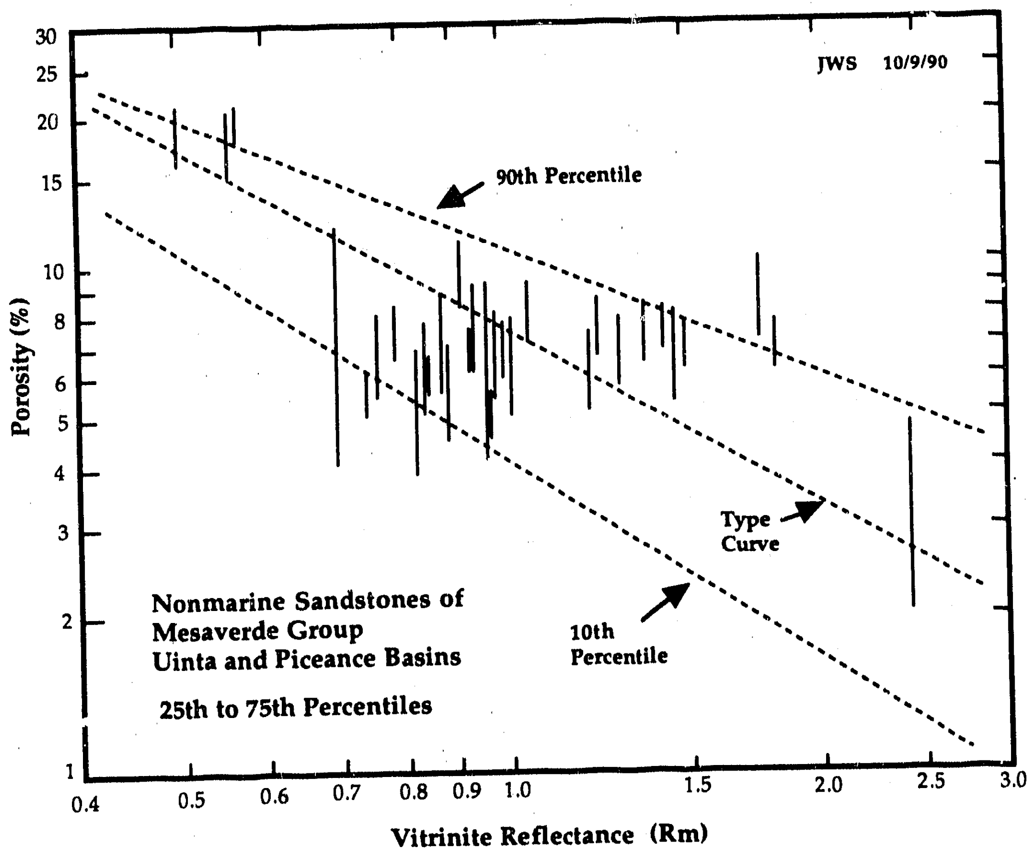

Figure 7. Plot of core-plug porosity versus vitrinite reflectance for 25th and 75th porosity percentiles (joined by vertical lines) of nonmarine sandstone intervals of Mesaverde Group, Uinta and Piceance Creek basins. Mesaverde data are compared to type curve and to 10th and 90th porosity percentiles representing sandstones in general (Schmoker and Gautier, 1989; Schmoker and Hester, 1990).

Drill Stem Test (DST) Analysis

Analysis of drill stem test data from 78 tests in wells in lower Tertiary and Upper Cretaceous hydrocarbon-producing domains in the Uinta Basin indicates that natural fractures provide major conduits to move fluids and gases to the wellbore in otherwise very low-permeability strata (Wesley, 1990). An evident lack of significant natural open fracture systems in impermeable strata of the southeastern part of the Uinta Basin has resulted in very low producibility. Many zones tested in deeply buried rocks below depths of 10,000 ft at Bluebell-Altamont oil field are naturally fractured. The permeability and radius of investigation in these rocks are relatively high, and the Horner-plot slope is low. Horner plots from DST's in and north of the large Red Wash field in the northeast Uinta Basin, especially for shallower alluvial rocks, exhibited low slopes associated with high permeability.

DST-derived permeability values for thick stratigraphic intervals of impermeable gas-bearing strata in the eastern part of the basin are very similar to permeability values derived from individual core samples. This is presumably due to the encasement of many individual Wasatch Formation reservoirs in relatively ductile claystone and the lack of numerous continuous open natural fracture systems in tight-gas formations in the eastern part of the basin which, if present, would most likely provide larger scale, higher permeability flow conduits.

Deeply buried overpressured strata are characterized by reservoirs whose core-derived matrix permeability values are near, and commonly below, 0.1 md and whose porosity values (most porosity being secondary) range from 5 to 10 percent. These strata contain open fractures and transmissivity (T = permeability x height) values through producing intervals are commonly high. Combined primary and secondary porosity values of 10 to 16 percent are common in normally pressured oil reservoirs and matrix permeability values may be as high as 1 d. Transmissivity values for such sequences can be relatively high because of their high matrix permeability.

Known tight gas-bearing sandstone reservoirs in the basin commonly contain porosity values ranging from 8 to 16 percent, but matrix and formation permeabilty values are 0.1 md or less. Transmissivity values for existing productive "tight gas" intervals are very low because of few natural open fractures.

SUMMARY

Analysis of gas in tight-gas rock reservoirs of the southeast part of the Uinta Basin indicate that the gas has migrated from underlying Upper Cretaceous source rocks through fractures and faults to overlying Tertiary and Upper Cretaceous strata. Petrographic and core analysis indicate values of porosity in rocks that have been heated to high temperatures will be quite low. Most fluid and gas migration is through fracture permeability paths. The volume of gas in reservoirs in the normally-pressured strata of the untested part of the basin may be optimized in those rocks along these migration pathways. Recoveries of gas will likely be limited in deeply buried rocks with few natural fractures because faults and fractures are probably necessary in many areas for both filling and draining the reservoirs.

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Systems Analysis of Low Permeability Natural Gas Formations in the Western United States

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Scott M. Klara
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OBJECTIVE

Systems analysis at the Morgantown Energy Technology Center (METC) is focused to support the United States Department of Energy's (DOE's) natural gas research program. Systems activities include developing and enhancing geologic models of basins containing low-permeability, gas-bearing formations, estimating in-place resources, and estimating recoverable gas volumes as a function of technology and wellhead sales price. Study results assist in defining and prioritizing research activities within the DOE. Ultimately, the analyses are structured to increase the percentage of United States' total gas supply produced from low-permeability formations.

BACKGROUND INFORMATION

Natural gas is viewed as the environmentally preferred fuel of the future because of its clean burning qualities. In addition, electric utility and industrial gas demand is expected to increase in response to new clean air legislation and regulations designed to address global warming. Given this outlook for gas, prospects for an annual gas demand of approximately 20 trillion standard cubic feet (Tcf) are favorable (DOE 1990).

Part of DOE's gas research effort addresses this increasing demand for natural gas. A considerable resource base resides in low-permeability formations but remains largely untapped because of its higher cost compared to "conventional" supplies. In order to effectively exploit the resource, estimates of both technically and economically recoverable gas volumes must be developed. In addition, as extraction technologies improve, e.g., horizontal wells, these technologies must be assessed with respect to their impact on the reserve base.

PROJECT DESCRIPTION

METC's systems methodology involves developing or updating geologic characterizations of select basins that are predominantly gas-bearing. The geologic characterizations include descriptions of structure, stratigraphy, and reservoir engineering properties. These data are collected from existing databases, published cross sections, etc., and provide the basis for estimating the in-place resource. The geologic descriptions are subsequently integrated with technology performance, cost, and financial analysis models. Collectively, the data, assessment models, and study results represent METC's systems analysis. Table 1 illustrates the methodology.

The adopted methodology is structured to allow significant flexibility in the analysis of low-permeability formations. Sensitivity analyses are conducted to quantify the influence of critical parameters, e.g., wellhead gas price and extraction technology, on the volume of recoverable gas. Figure 1 shows results from these types of studies.

Table 1. Systems Analysis Methodology
(after ICF Resources 1990)

INPUT	MODEL	OUTPUT
-Reservoir Properties	GEOLOGY	-Gas-in-place
-Stimulation Design -Production Practices	PRODUCTION	-Production Streams
-Reservoir/Production Properties -Cost Region	COSTING	-Drilling & Completion, Stimulation, Equipment, -Operations Costs
-Production Streams -Engineering Costs -Gas Prices, Taxes	ECONOMICS	-Discounted Cash Flow -Financial Performance

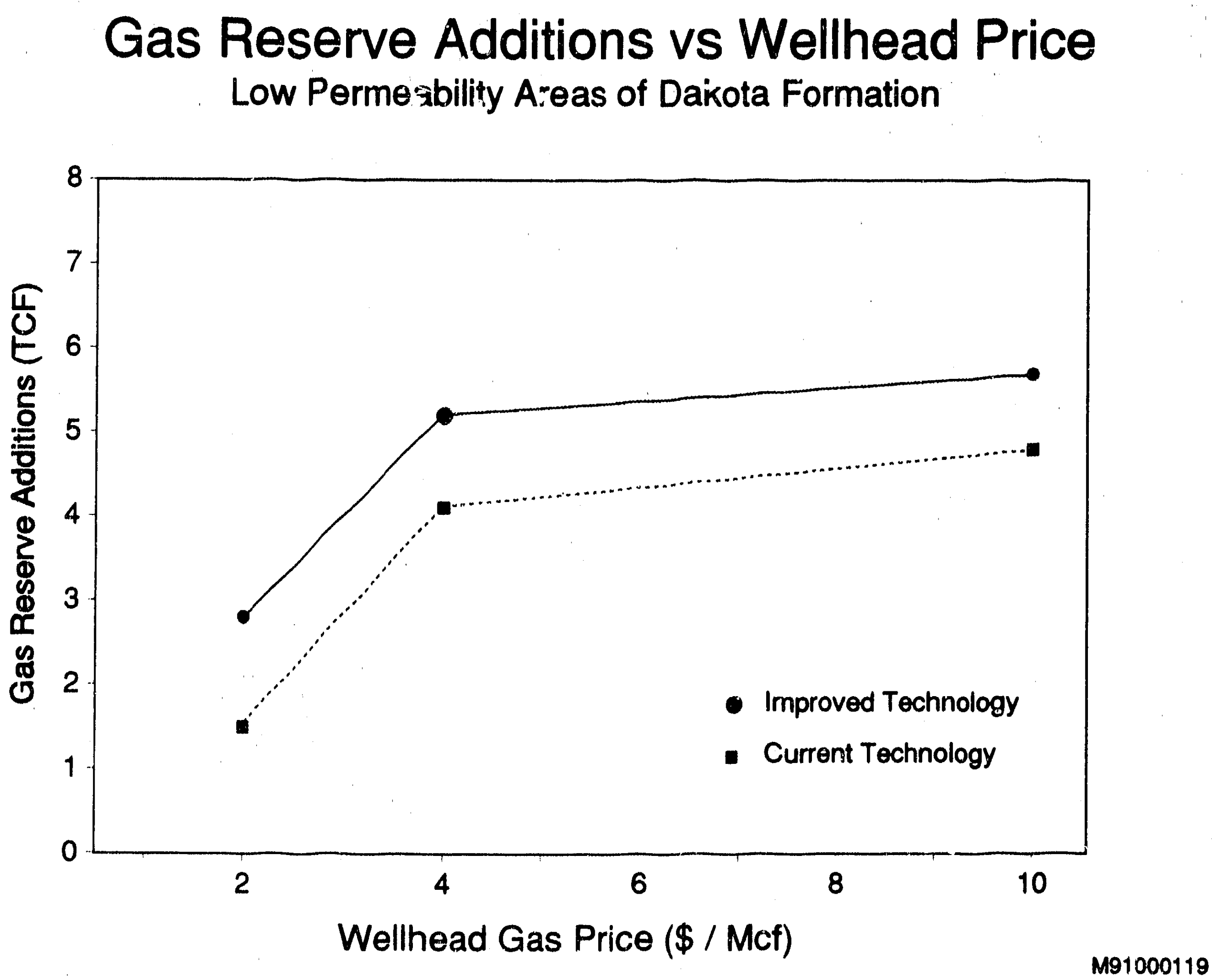

Figure 1. Typical Technology Assessment Results

Recent activities have focused on the Washakie and San Juan Basins. Figures 2 and 3 show the locations of these basins in Wyoming and in New Mexico and Colorado. The Washakie Basin, a subbasin of the Greater Green River Basin (GGRB), is being evaluated because of its resource potential. A recent estimate of the GGRB's in-place resource is more than 5,000 Tcf (United States Geological Survey [USGS] 1988).

It is imperative that estimates of recoverable gas be developed for current completion strategies and prevailing gas prices. Assessment of improved technologies must also be completed, which may lead to significant reserve additions.

Natural gas potential from the San Juan Basin is largely unknown with respect to new or improved technologies such as horizontal drilling. Gas demand in areas supplied by the San Juan Basin is expected to increase over the next several years. Competing markets for San Juan Basin supplies are (1) the cogeneration and enhanced oil recovery industries in California, and (2) an anticipated demand increase for west Texas (ICF 1990).

RESULTS

Washakie Basin Analysis

Analysis of the Washakie Basin has progressed to where geologic and engineering data are available for technology assessment studies. Cross-sections and other geological data have been collected and updated. Geophysical well logs have been analyzed to determine reservoir engineering data such as porosity and fluid saturations.

The basin has been partitioned into more than 230 units of analysis, and area-weighted properties have been assigned to each unit. This methodology has been used for each of five formations of interest underlying the Washakie Basin. In addition, for areas where data are not available, values for typically exhibited data trends have been assigned. Determination of the in-place resource and available reserves is currently underway. Analysis of improved extraction technologies will be completed as planned.

Other subbasins within the GGRB are also being characterized in terms of geology and engineering parameters. In the end, aggregation of the data and results for the entire GGRB will be compared to the in-place resource reported by the USGS (Law, et al 1989). Along these lines, the in-place resource for the Washakie Basin has been "derived" from the USGS' study of the GGRB. This derivation indicates an in-place gas volume of 1,070 Tcf with more than 600 Tcf "locked" within the Mesaverde Formation. Comparison of METC's forthcoming Washakie Basin resource estimate to the USGS' is anticipated for the next quarter.

San Juan Basin Analysis

The San Juan Basin covers 7,500 to 10,000 square miles. It is approximately 100 miles in diameter and encompasses parts of six counties. The formations underlying the basin are generally continuous throughout. Five, low-permeability, gas-bearing formations underlying the San Juan Basin were evaluated for their supply potential. These formations are (1) Dakota, (2) Mesaverde (Point Lookout and Cliff House Sandstones), (3) Chacra, (4) Pictured Cliffs, and (5) Fruitland.

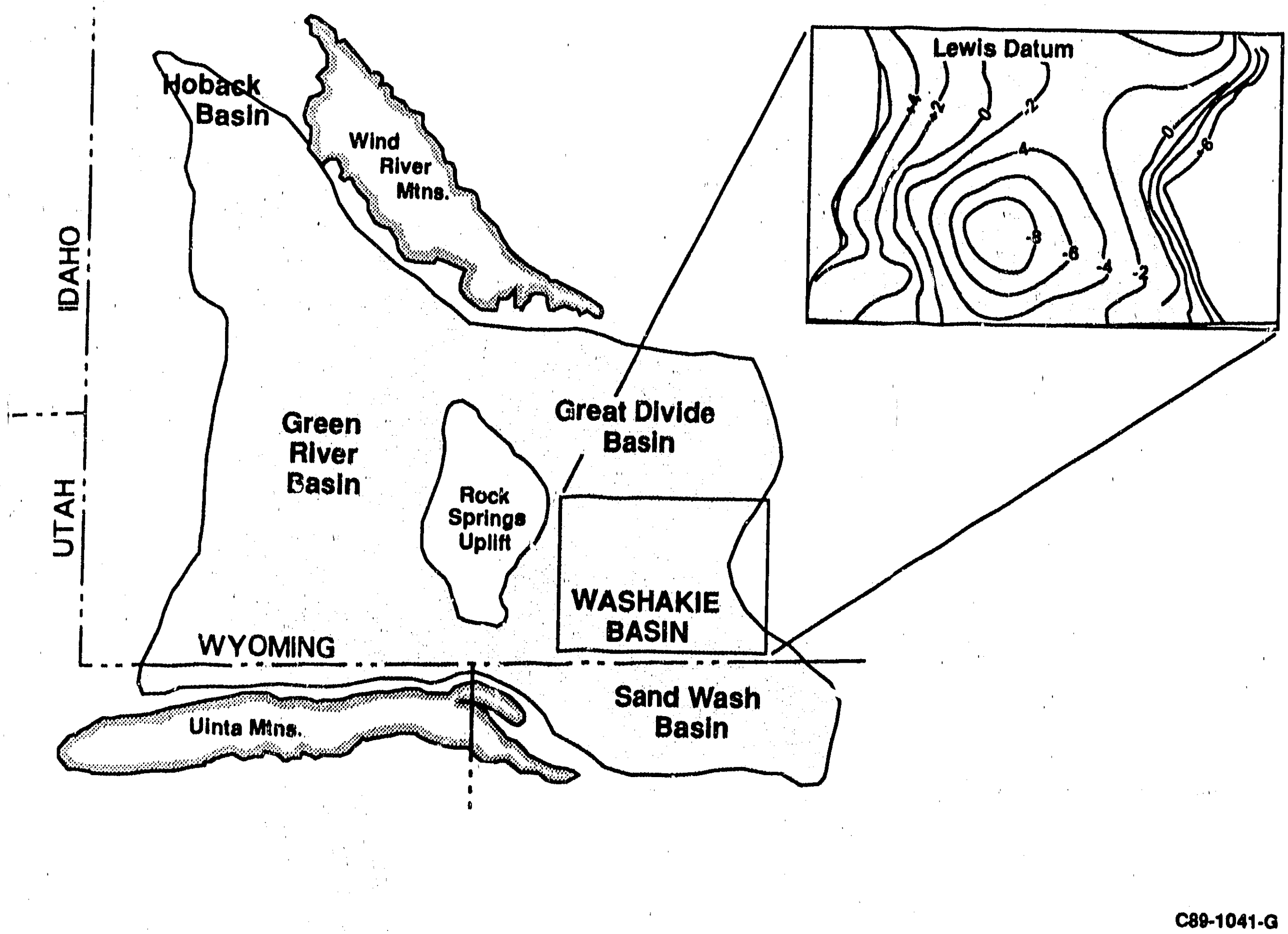

Figure 2. Washakie Basin Study Area (Greater Green River Basin Stippled)

Initial analysis has been completed on a disaggregate basis, i.e., wells are assumed to penetrate and produce from a single formation even if several formations overlie one another. This assumption skews the study results because more than one formation can be accessed from a single wellbore (commingled). Methodology changes are being implemented at this time to include commingling or "stacking".

Although the main focus of the San Juan Basin analysis is low-permeability formations, higher permeability (conventional) areas were also analyzed. Resource estimates were determined for each formation (all permeability values) as well as the low-permeability areas (less than 0.1 millidarcy [md]). Gas-in-place for the entire basin is estimated to be 66.3 Tcf with 17.1 Tcf of this total coming from low-permeability areas.

Two fracturing technologies were assessed in the study: a base case (current) technology and an improved stimulation case. The base case represents typically pumped hydraulic fracture treatments, while the improved stimulation

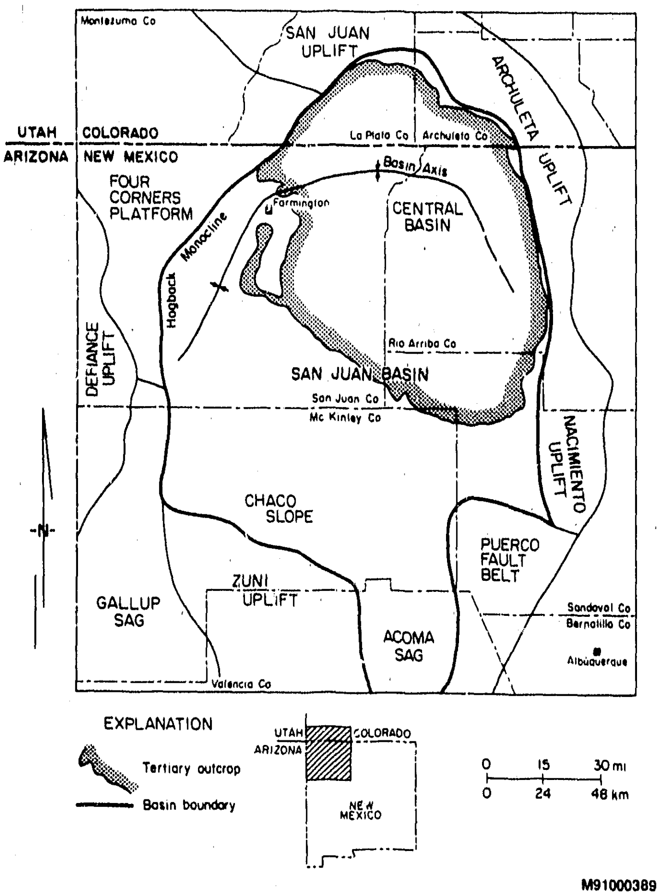

Figure 3. Location and Generalized Structure of the San Juan Basin

represents a longer, more conductive fracture. Specifics of these two assessed technologies are listed in Table 2.

Technically recoverable gas for the low-permeability areas of the basin has been estimated to be about 7.0 Tcf for the base technology scenario and more than 8.0 Tcf for the advanced technology scenario. For the base technology, economical reserve additions from the low-permeability areas of the basin are estimated to be 2.1 Tcf at a wellhead gas price of $2/thousand standard cubic feet (Mcf). Details of the reserve study (current technology) are listed in Table 3.

Assessment of improved stimulation for recovering natural gas from the San Juan Basin indicates the following:

- economically recoverable gas (@ $2/Mcf) can be increased by more than 80% (an additional 1.7 Tcf) from low-permeability areas

- more than 80% of the incremental reserve additions are present in the Dakota Formation (1.4 Tcf of the 1.7 Tcf)

- gas recoverable from the low-permeability areas of all five formations (@ $4/Mcf) is estimated to be 30% more than the base case volume.

This analysis confirms that at lower wellhead gas prices (prevailing prices), improved technologies have significant potential for increasing natural gas reserves.

FUTURE WORK

Methodology changes are being implemented that will allow assessment of "stacked" formations (commingled production) and horizontal well technology. The stacking option should improve the economics for a given scenar'o by allowing a single well to be completed in more than one formation. The Washakie and San Juan Basins will be re-assessed when these capabilities are operational.

In addition, systems analysis will continue to focus on basins that have significant gas potential. Fiscal Year 91 efforts include evaluation of the Red Desert and Sand Wash Basins (part of the Greater Green River Basin). Analyses of these basins, in association with the Washakie Basin activities, will result in approximately 60% of the GGRB being assessed.

Table 2. Technology Parameters

Parameter	Base Technology	Advanced Technology
- Fracture Wing-Length	200 ft	600 ft
- Fracture Conductivity	200 md/ft	1000 md/ft
- Drainage Area	160 acres	160 acres
- Fluid Efficiency	60%	80%

Table 3. Estimated Reserves Additions for the San Juan Basin (Base Technology, Low-Permeability Areas)

Formation	$2/Mcf	$4/Mcf
Pictured Cliffs	0.67 Tcf	1.00 Tcf
Dakota	1.41 Tcf	4.06 Tcf
Cliff House	0.00 Tcf	0.07 Tcf
Point Lookout	0.00 Tcf	0.47 Tcf
Chacra	0.00 Tcf	0.00 Tcf
Basin Total	2.08 Tcf	5.60 Tcf

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Geotechnology for Low-Permeability Gas Reservoirs

CONTRACT INFORMATION

Contract Number	DE-AC04-76DP00789
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Period of Performance	October, 1988 - continuing

Schedule and Milestones

FY90 Program Schedule

	O	N	D	J	F	M	A	M	J	J	A	S
Lab Studies	—	—	—	—	—	—	—	—	—	—	—	—
MWX Extrapolation			—	—	—	—					—	—
Expert System						—	—	—	—	—	—	—
Analysis SHCT-1					—				—	—	—	—

OBJECTIVES

This project provides geotechnical support to the Department of Energy's Western Gas Sands Subprogram. The approach is to use existing geotechnical capabilities and the broad base of results and expertise from the Multiwell Experiment and apply them in areas of sedimentology and natural fractures, geomechanics and in situ stress, and stimulation.

BACKGROUND INFORMATION

Sandia's experience in low-permeability natural-gas reservoirs, derived from studies at the Department of Energy's Multiwell Experiment (MWX), is being used to (1) extrapolate techniques for reservoir characterizations and stimulation to other parts of the Piceance basin, (2) transfer MWX technology to commercial operators addressing similar problems, and (3) assess new data from the Slant Hole Completion Test at the MWX site. Results from the four tasks of this project are given in the next section.

PROJECT DESCRIPTION AND RESULTS

Extrapolation of MWX Results

Oriented core from two wells in the Piceance basin has been examined, as part of DOE's program to test the applicability of the results of the Multiwell Experiment to other parts of the basin. These two wells were drilled by Barrett Energy and Fuelco, with the core being contracted for by CER Corporation as an agent of DOE. Results of the program support and extend the findings of the MWX studies in regard to in situ stresses and natural fractures.

Fractures. In both wells, the natural fractures are mineralized, and occur in unidirectional sets that are confined to the sandstone and siltstone beds. Fracture trend of four fractures in core from the Barrett well, 12 miles west of the MWX site, parallels the west-northwest trend seen in MWX core (Fig. 1).

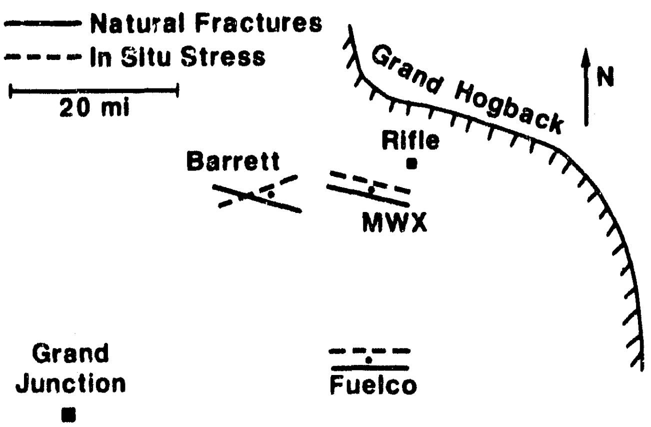

Figure 1. Stresses and Fractures in Wells

The dominant trend of 16 fractures in the Fuelco well, which is located about 22 miles south of MWX and in a different fracture domain, is more nearly east-west. This latter trend is not unexpected, as it conforms to fracture trends found in nearby outcrops and to the stress trend predicted for this part of the basin on the basis of models of indentation tectonics.

Stress. Stress orientations in the core were derived from measurements of petal fracture strikes and velocity anisotropy. Preliminary data suggest that the horizontal maximum stress in the Fuelco well parallels the natural fracture trend, in accordance with predictions. The stress orientation in the Barrett well, however, is 20-40° oblique to the natural fractures. This apparently anomalous relationship is explainable in terms of a secondary topographic stress effect, similar to that seen on a smaller scale at the MWX site, resulting from the local high-relief terrain.

Analysis of SHCT-1 Core

Core from DOE's Slant Hole Completion Test well (SHCT-1) was analysed for the purpose of characterizing natural fractures. About 236 ft of 4-inch diameter core was recovered from the paludal zone, and 113 ft of 2 5/8-inch diameter core was recovered from the Cozzette sandstone. The wellbore was deviated 60° from the vertical in the paludal zone, and about 85° from vertical in the Cozzette. The deviated wellbore azimuth was within a few degrees of true north, and thus was perpendicular to the dominant fracture trend.

Paludal zone. Thirty-one mineralized fractures were observed in the paludal core (Fig. 2). All but two of these

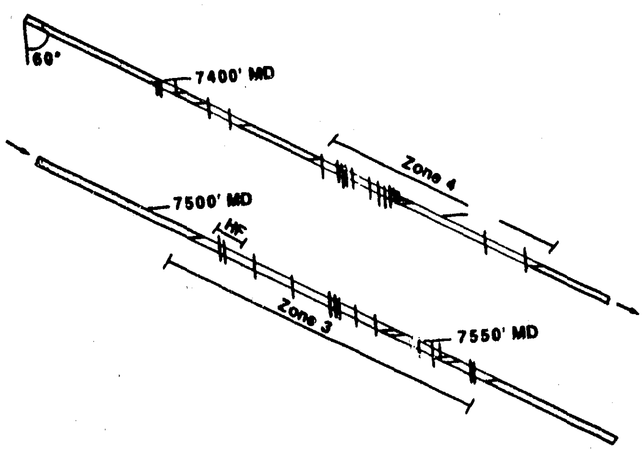

Figure 2. Natural Fractures in Paludal Zone, SHCT-1

strike west to west-northwest. Mineralization is quartz and/or calcite, quartz being the earlier phase where both are present. Common euhedral crystal faces indicate locally open fractures at depth. Fracture spacing averages 2.2 ft, and is independent of sandstone host-bed thickness. Fracture spacing ranges from less than 0.1 ft to 6 ft, but fractures can be grouped into "swarms" that are spaced 4.8 ft on average (min 2.5 ft, max 7.8 ft).

Cozzette Sandstone. Thirty-seven mineralized natural fractures were observed in the Cozzette core (Fig. 3)

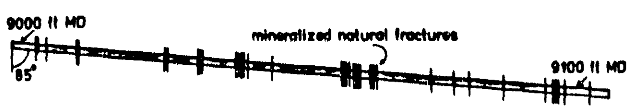

Figure 3. Natural Fractures in Cozzette, SHCT-1

giving rise to an average spacing of 3 ft (min. <0.1 ft, max 17.5 ft). Again, swarms are the normal mode of occurrence, where swarms are spaced 4 to 17.6 ft apart, with an average of 9 ft. Fractures in the Cozzette may contain both calcite and quartz (as in the paludal zone), but quartz is more dominant and better developed. Quartz is again the early phase where both minerals are present. Open-fracture permeability is indicated by euhedral mineral forms, as well as by cored cohesive fractures with visible remnant apertures. Fracture trends are more nearly east-west in this part of the hole.

It is interesting to note that although fracturing was noted in thin-bedded, sandstones and siltstones in vertical core from the three MWX holes, vertical core encountered only one vertical fracture within 175 ft of actual reservoir rock (paludal zones 3, 4 and the Cozzette) cut at this same site where deviated core shows 68 such fractures.

Cored hydraulic fracture. A 4 1/2 ft long (measured depth) interval of slant-hole core from paludal zone 4 shows a region of intense unmineralized fracturing. Testing is still in progress, but preliminary indications are that this is the zone penetrated by a MWX hydraulic stimulation fracture, and that the multiple fractures are strands of this hydraulic fracture. The strands contain no obvious sand proppant, but are located near the top of the fractured interval. There are indications of gel residue on the fracture surfaces. The unmineralized fractures are sometimes en echelon and incompletely separate the rock. Most of the strands parallel the mineralized, obviously natural fractures found in the same interval.

Laboratory Studies

The effective stress law of a material defines a relation between confining stress and internal pore pressure for a given process or property. Effective stress laws are usually modeled in the form

$$\text{property} = G(\sigma - \alpha p),$$

where property (or process) includes both permeability and deformation. G() is a generalized function describing the effect of stress on the property, σ is the confining stress on the sample, p is the pore pressure, and α is the poroelastic parameter that relates stress and pore pressure. While α is usually taken to be constant, which gives a linear effective stress law, there is no reason a priori to assume that it does not vary with either σ or p. Sandia's study has investigated this possible variability.

The laboratory apparatus consists of an overburden coreholder, input and output pressure transducers, output flowmeters, a high pressure nitrogen source for pore pressure, a hydraulic fluid pump for confining stress, and strain gage circuitry. Permeability measurements were made using the steady state technique. Strains were measured with strain gages expoxied to the samples, with leads exiting through the jackets and out the feedthroughs. Prior to testing, all of the samples were put through a seasoning process (i.e., pressure cycling[1]) to close some of the relaxation microcracks and give a non-variable rock sample.

The analysis technique that was used for this study[1] is the response surface method as developed by Box and Draper.[2] In applying the response surface technique, we assume that nothing is known of the material behavior and we empirically build a model by fitting an approximate surface (the response surface) to the data. The parameters describing the response surface can then be examined to deduce information about material behavior. This approach is particularly useful for tight rocks with relaxation microcracks that induce significant nonlinearity into the material behavior. Such nonlinearity invalidates any mechanistic or constitutive models based on linear elasticity.

The first sample tested was a sandstone from the coastal interval of the non-marine Mesaverde, cored at the Multiwell Experiment (MWX) at a depth of 6520 ft. We chose this particular sample because it has the lowest permeability (a few microdarcies, dry) of any of the tight MWX sandstones and it had a sizable velocity anisotropy (18%) due to a preferentially oriented relaxation microcracks. We considered both of these features to be worst case scenarios in determining effective-stress-law parameters. To investigate the effects of anisotropy, two samples were tested, both horizontally plugged. One sample (6520P) was parallel to the maximum stress and thus perpendicular to the axis of the maximum number of microcracks; the second sample (6520N) was normal to the maximum stress and parallel to the axis of the maximum number of microcracks.

The data for the permeability results of samples 6520N and 6520P are shown in the 3-dimensional plots in Figure 4 for loading cycles. These plots show the surface in k-σ-p space, with lines of constant pore pressure and constant permeability superposed. the constant pore pressure lines are the ones along which the data were obtained. These plots show how well

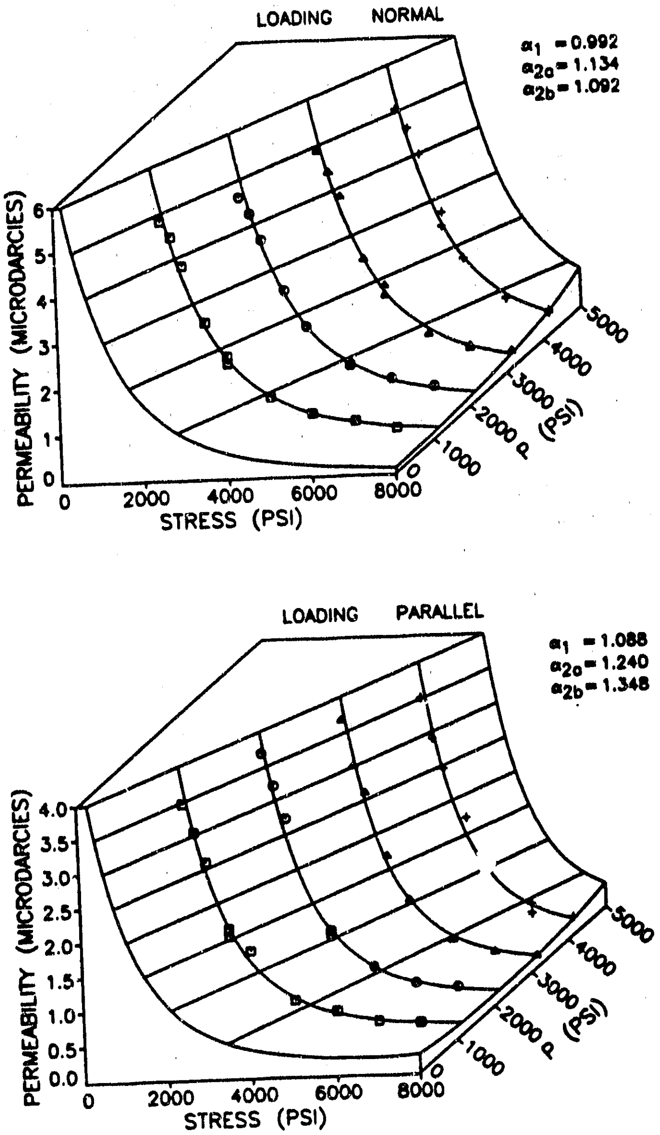

Figure 4. Inverse Permeability Response Curves, (Bottom) 6520P & 6520N (Top), for loading

the response surface fits the data. In this case we find that the effective stress law has some nonlinearity with first-order α values (α_1) of 0.99 for the normal sample and 1.09 for the parallel sample.

The volumetric strain results for sample 6520N are given in the ε-σ-p inverse-response-surface plots shown in Figure 5 for both loading and

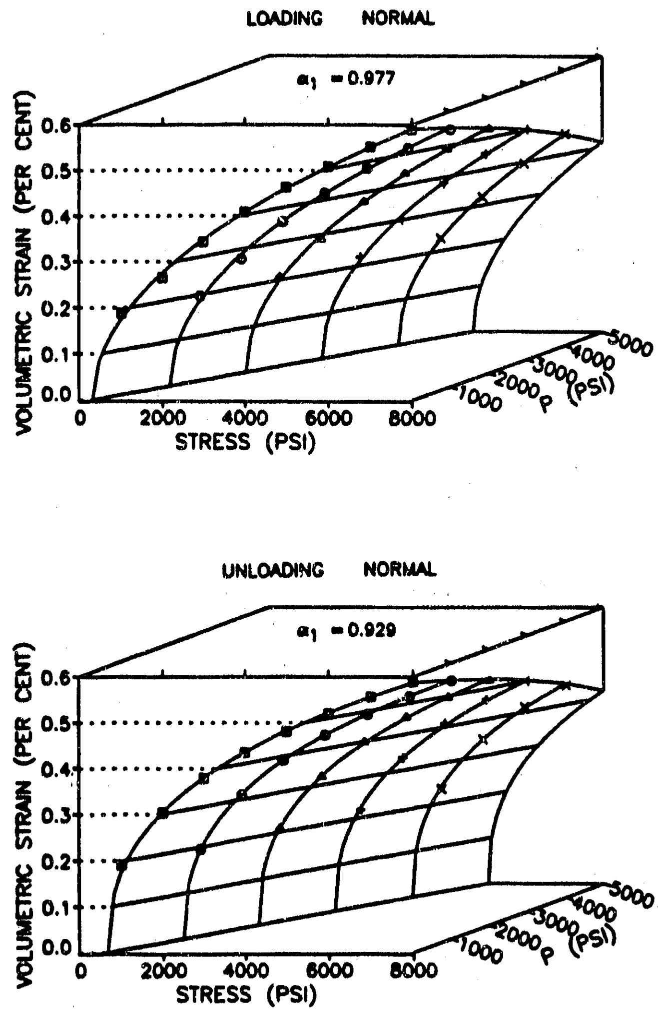

Figure 5. Inverse Deformation Response Curves, 6520N

unloading cycles. As with the permeability data, these samples were seasoned prior to testing. The overall strain behavior is highly nonlinear, undoubtedly because of closure of the microcracks and slot porosity typical of this tight sandstone. In all cases the response surfaces provide excellent fits of the data.

The response surfaces generated by the statistical analyses can be used to determine the variability of α over the data domain. This is achieved by determining the stress/pressure functionality of the approximate response surface over the region of interest and can be plotted as a surface in α-σ-p space, as shown in Figure 6 for permeability of the two

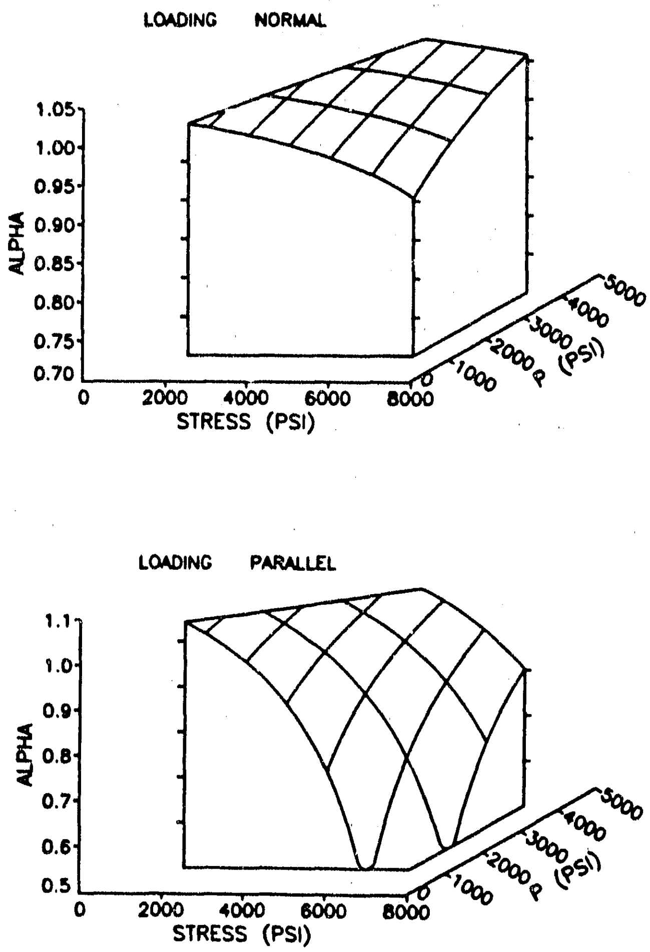

Figure 6. α Permeability Surfaces, 6520N (Top) & 6520P (Bottom), for Loading

coastal sandstone samples (6520P and 6520N) in loading. For sample 6520N, the α surface is relatively constant, and α is approximately unity throughout the data domain. For the parallel sample, however, the α surface is much more complex and α tends to fall off at the high-stress, low-pressure corner. Some of this fall off may be due to measurement error and to lack of constraint on the surface at a corner, but the general trend is evident throughout the data domain.

For deformation, or volume strain, the results are more consistent but we find that they disagree with theoretical values. Figure 7 shows

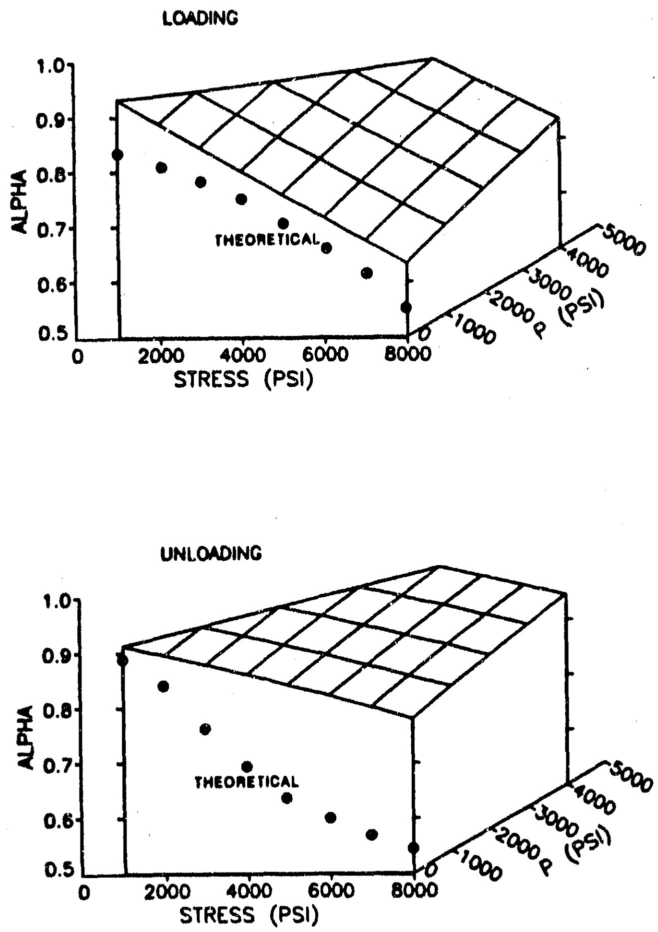

Figure 7. α Surfaces for Deformation

the α-σ-p surfaces for plug 6520N in both loading and unloading, as well as the theoretical value of α as determined from our volume strain data with zero pore pressure and a measured, unjacketed modulus of the rock sample. The α surface is found to decrease with increasing stress and increase with increasing pore pressure, with α starting at the first-order (α_1) value at low stress/pressure conditions. The surface is relatively planar in both cases and α varies from 0.65 to 0.94 during loading and 0.76 to 0.92 during unloading, indicating a path dependency in the value of α. While we generally caution against trying to extrapolate the response surface outside of the data domain, the α surface is so planar that an extrapolation to reservoir conditions (σ=6500 psi; p=4500 psi) is justified, yielding an estimated in situ α of 0.92 for this sample (using the unloading data).

A second sample tested was from the Rollins sandstone, a marine Mesaverde sandstone from a depth of 7560 ft at the MWX site. This sample showed a much smaller velocity anisotropy than the coastal sandstone (about 5%), so plugs were only tested in one orientation (parallel to the maximum horizontal stress). The value of α for deformation varies only slightly with stress, but more so with pore pressure, ranging from 0.73 to 0.95 over the data domain and shows poor agreement with the calculated values. The extrapolated value of α to reservoir conditions (σ=7300 psi; p=5600 psi) yields a value of 0.98. No permeability tests were performed on this sample.

Expert System: SAGE (Sandia Advisor for Gas Extraction)

SAGE is a workstation-based information system designed to give accurate and reliable advice on stimulating natural gas production from tight sand reservoirs. The purpose of SAGE is to make the expertise and knowledge obtained during the Multiwell Experiment available in a field tool.

SAGE uses guided information retrieval to classify a well from its core and well log data, production history, etc. Once the attributes of a well are known, the appropriate stimulation technique can be suggested. Rules, a geological taxonomy, knowledge about materials, and the current state of its own problem-specific information (in particular, its current goals) determine what information SAGE requires at any given time. If SAGE cannot directly access or indirectly deduce information needed to reach its current goal because it lacks data, it asks the operator for the data. Conversely, the operator can enter data he knows to be important at any time. The interface explains its conclusions and can illustrate its current information state both pictorially and taxonomically (Figure 8). The results of an on-line session can be saved and recalled. SAGE also provides on-line documentation. Future work includes broadening SAGE knowledge and recommending simulation techniques based on lithology, deposition environment, stress direction, etc.

The primary deductive mechanism in SAGE is backward chaining into an object-oriented data set that captures what is currently known about the well being examined. The name "backward chaining" comes from the ability to follow a "chain" of if-then rules from the conclusion of interest "backward" to the supporting evidence. For example, suppose SAGE is trying to determine whether the effective permeability of a well is significantly higher than the permeability of the matrix rock. There is a rule in SAGE that implies that: IF there is a sufficiently

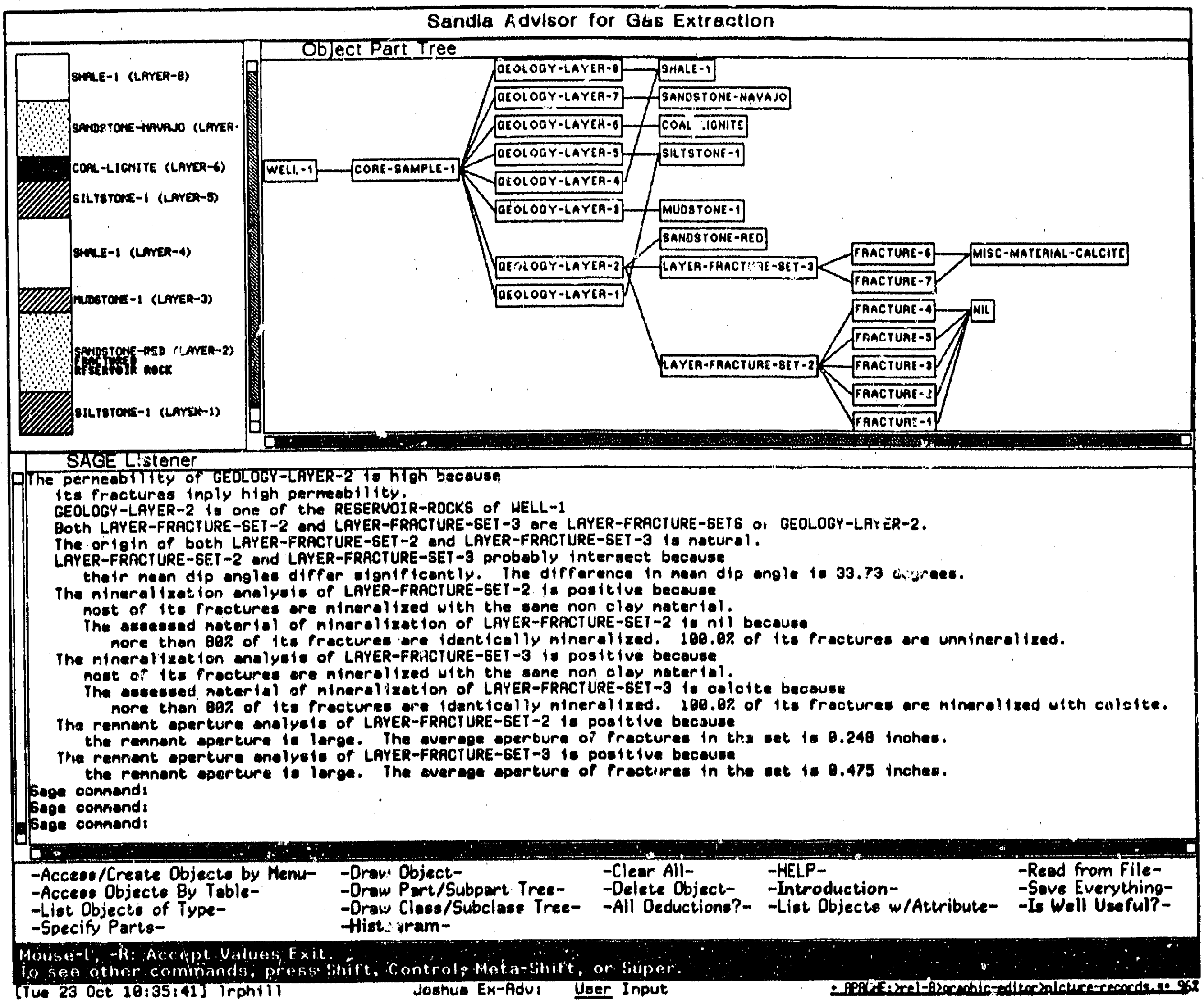

Figure 8. The SAGE Screen in Use

multidirectional group of fractures in the reservoir rock that are significantly large and appropriately mineralized (or non-mineralized), THEN the effective permeability is likely to be high. SAGE examines its knowledge base, looking for fractures associated with the well. If there are such fractures, and SAGE can determine that they are in the reservoir rock, it then attempts to determine how they are mineralized, etc. SAGE first looks to see whether they information it seeks is already in its local database. If it isn't SAGE either:

1. Asks the operator for the information, if it has been

previously told the operator may know, or

2. Looks for another rule whose conclusion would supply the information if that rule's antecedents were true, and attempts to find or deduce those antecedents (the chaining behavior), or

3. Fails to deduce the conclusion of the rule.

Backward chaining allows several different explanations for the same conclusion, which is important for this problem because of the potential for unknowns, and once a conclusion is found, produces it without further search.

The general attributes needed to predict economic feasibility are understood (marine environments are more likely to be economically productive than non-marine; fractures with apertures are more likely to increase effective permeability than fractures with; a stress field oblique to existing fractures is better than one that is parallel; etc.), but all the nominal conclusions can be in error in some conditions, and none of the questions have black and white answers. In addition, many of the wells in question are the marginal cases that were (or will be) abandoned because they don't readily meet current producibility requirements or respond to today's set of useable techniques. By giving appropriate weight to all of the various factors and considering them simultaneously, SAGE will determine which stimulation techniques have the best chance of working on a given well and predicting how well they should work.

FUTURE WORK

As plans are made for more wells of opportunity, Sandia will continue to assist in core analysis, especially in regard to fractures and in situ stresses. The SHCT-1 core will be carefully examined for fracture characterization, and the fracture spacings will be quantified. Future laboratory experiments will complete measurements of the deformation and permeability α parameters in all four depositional environments/types of reservior encountered in the Mesaverde Formation at the MWX site. Finally, the expert system will continue to be modified and refined until it is in an easily useable form where it will aid in the transfer of MWX technology to industry.

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An Evaluation of Co-Planar Lineament Analysis and Some Thoughts on Using Surface Geological Data to Predict Subsurface Geology

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INTRODUCTION

This study is an evaluation of the usefulness to natural gas exploration and development of a computerized method of mapping lineaments on the Earth's surface. The lineament mapping technique discussed in this paper is known as co-planar lineament analysis, and was developed by Eliason (1984).

An attempt has been made to establish a correlation between lineaments at the Earth's surface, which may indicate fracturing of the surface rock, and fractures in natural gas producing rocks below the Earth's surface. A cheap and accurate way to predict fracturing of gas reservoir rock is of interest because fractures greatly enhance the productivity and economic viability of a gas well, particularly those gas wells that produce gas from sandstones of low permeability.

The Douglas Creek Arch was chosen for this study because of its long history of gas production from nearly 500 fairly dense and uniformly spaced wells in the Mancos B Sandstone. These factors were considered necessary to detect linear trends resulting from fracture-enhanced permeability and porosity on contour maps of initial and cumulative production. Also, because the average production interval is rather shallow (2,800 feet) and because the surface rocks do not differ greatly in age from the gas producing rocks, it was thought that this area would be a good one in which to use remote sensing or surface measurements of fractures to aid in detecting linear surface features associated with production-enhancing fractures in the reservoir rocks. The shallow depth and similarity in age of the surface and reservoir rocks should favor the possibility that fractures or lineaments measured at the surface correspond to fractures in the reservoir.

GEOLOGY OF THE DOUGLAS CREEK ARCH

The Douglas Creek Arch is a broad, north-south trending anticlinal structure located in northwestern Colorado, to the west and north of the city of Grand Junction. The arch separates the Piceance Basin (east) from the Uinta Basin (west) (Figure 1). Many northeast trending normal faults are exposed at the surface (Figure 2) along the Douglas Creek Arch (Tweto 1979). According to Kellogg (1977), these faults dip 75 to 80° and have vertical displacements at the surface as great as 1,000 feet; however, most show less than 500 feet of offset. Johnson and Finn (1986) believe the age of these faults is post-Late Eocene because rocks of Late Eocene age that are cut by the faults show no thickness change across the faults.

In addition to the northeast set of normal faults exposed at the surface, many northwest trending normal faults are noted in the subsurface on seismic lines in the area (Waechter and Johnson 1985, 1986). These faults are

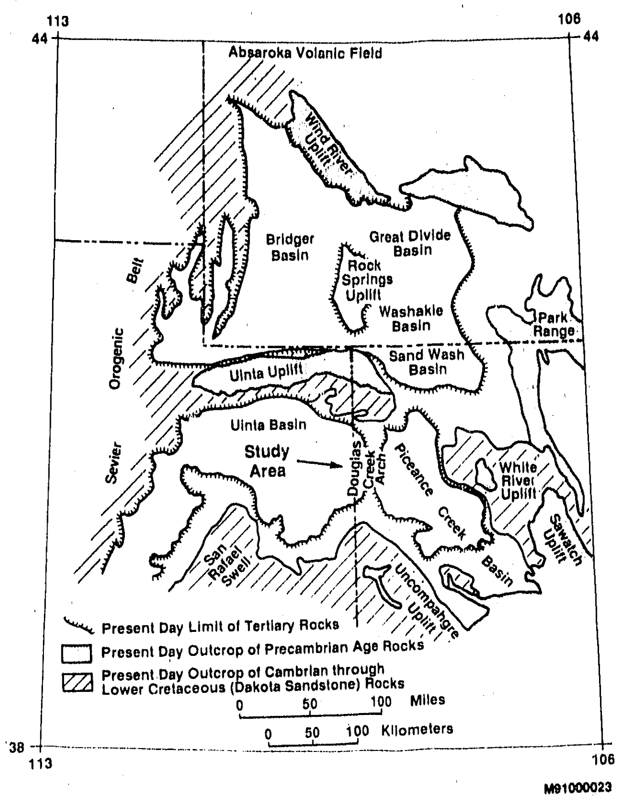

Figure 1. Index Map Showing Location of the Douglas Creek Arch and Surrounding Uplifts and Basins (Johnson and Finn 1986)

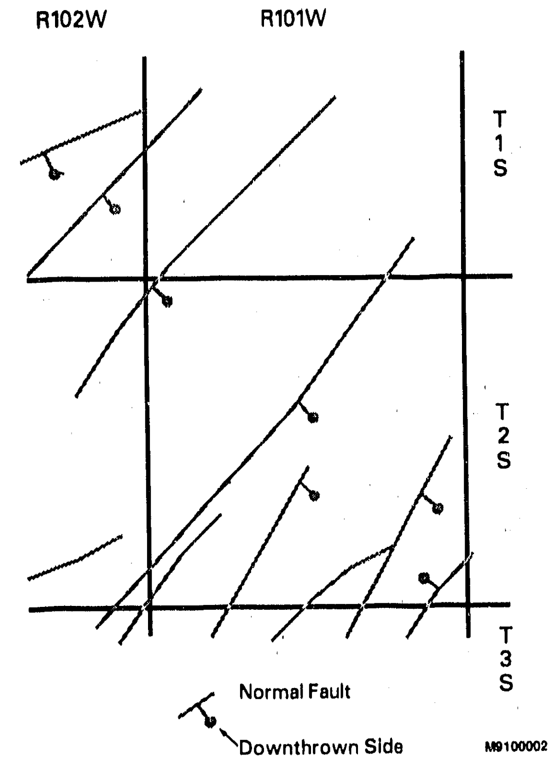

Figure 2. Portion of the State Geologic Map of Colorado (Tweto 1979)

nearly vertical and cut the basement rocks, but most seem to die out in the Pennsylvanian-to Permian-age Maroon Formation, and therefore, do not appear to cut the Mesozoic rocks in the area (Waechter and Johnson 1986).

The primary gas reservoir on the Douglas Creek Arch is the Upper Cretaceous Mancos B sandstone. Through the end of 1987, this formation had produced slightly over 298 billion cubic feet of gas from 481 wells. Kellogg (1977) and Witherbee, Godfrey, and Dimelow (1983) describe the formation as a series of interbedded marine claystones, siltstones, and fine sandstones that are overlain and underlain by the marine Mancos Shale. Coalson, Duey, and Kellogg (1982) report that the average porosity of the reservoir is 9 to 12% on logs and 10 to 11% in cores, and that the permeability averages 0.1 md. The depositional environment is discussed by Matheny and Picard (1985), Fouch et al. (1983), Witherbee, Godfrey, and Dimelow (1983), Swift et al. (1987), and Lorenz and Muhr (1989).

CO-PLANAR LINEAMENT ANALYSIS

Co-planar lineament analysis uses digital topographic data to analyze stream valleys and other topographical depressions that are linear for more than 400 feet. The assumption behind the technique is that erosion takes the path of least resistance and, given a more or less uniform bedrock formation, erosion occurs most readily along fractures or zones of fractures. Topographic lows such as stream valleys are areas where erosion has been most effective; therefore, a linear feature may be the result of fracture control of erosion.

Once the topographic data have been acquired, they are input into computer memory, and vectors are determined from topographic lows. The vectors are those approximately straight line segments running through contour Vs and having lengths of at least 400 feet. The computer then performs calculations on each pair of vectors to determine whether the vectors are in the same plane. If the two vectors are found to be co-planar, a plane is thus identified. Since a plane is identified and not just a lineament, the dip of the plane is determined, in addition to its strike and its location on the Earth's surface.

The technique can use several types of digital topographic data. It can use topographic contours digitized from topographic maps such as the standard 7.5-minute U.S. Geological Survey maps, or topographic data acquired by satellites and known as Digital Elevation Models for these same 7.5-minute quadrangles, which are available on magnetic tape from the U.S. Geological Survey. The data tapes used in this study were sent to Dr. Jay Eliason of Geological Consulting and Analysis Services of Deary, Idaho, for a co-planar lineament analysis. The results of his study are shown in Figures 3 through 5.

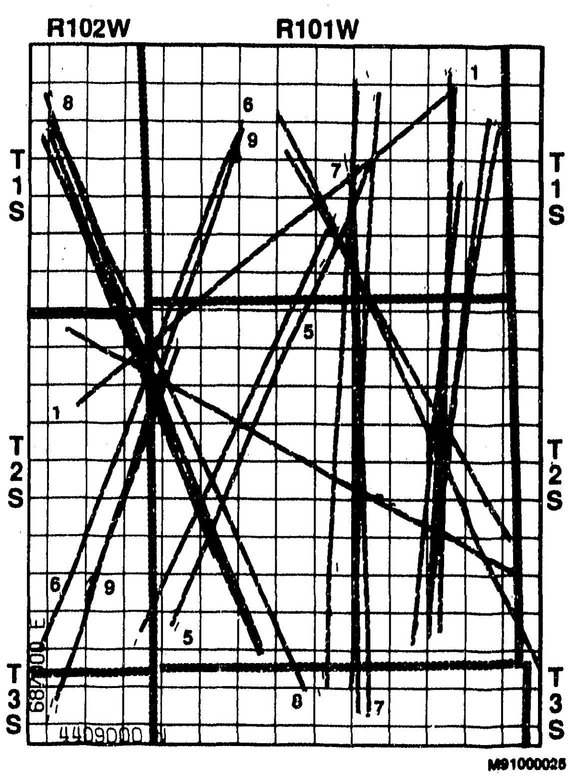

Figure 3. Map Showing the Orientation and Location of Major Plane Sets Determined by Co-Planar Lineament Analysis

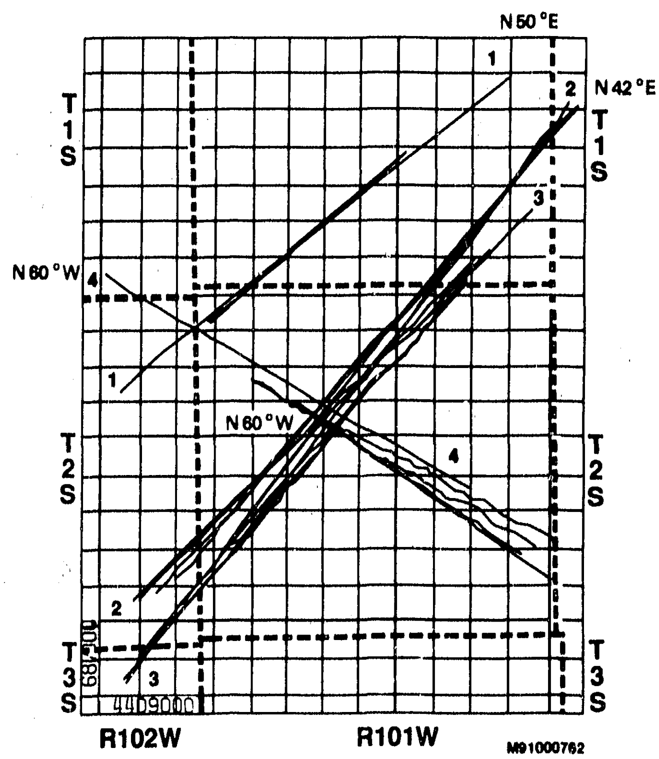

Figure 4. Map Showing the Orientation of Secondary Planes Determined by Co-Planar Lineament Analysis

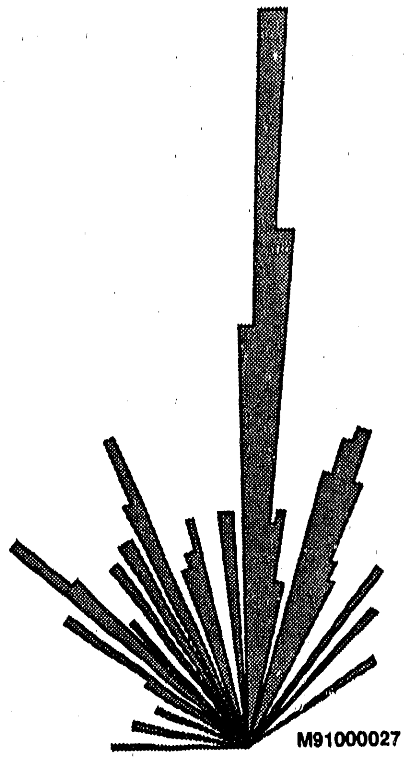

Figure 5. Rose Diagram of Planes Determined by Co-Planar Lineament Analysis

The co-planar lineament analysis was conducted over all of T2S-R101W, most of T1S-R101W, and portions of the townships that abut these two on the west and south (Figure 6). The area selected for study is where the least productive Mancos B wells are located (lower cumulative production on Figure 7 and lower initial production on Figure 8). These wells are poor producers presumably because of low permeability and porosity. Therefore, it is assumed that linear trends of wells having better production in the area of generally poor production (see Figures 7 and 8) are probably good producers because of fracture enhancement of reservoir permeability.

The vectors selected by the computer are displayed in Figure 6. The dominant plane sets (i.e., the co-planar lineaments), which are averages of several individual planes having nearly the same location, strike, and dip, are

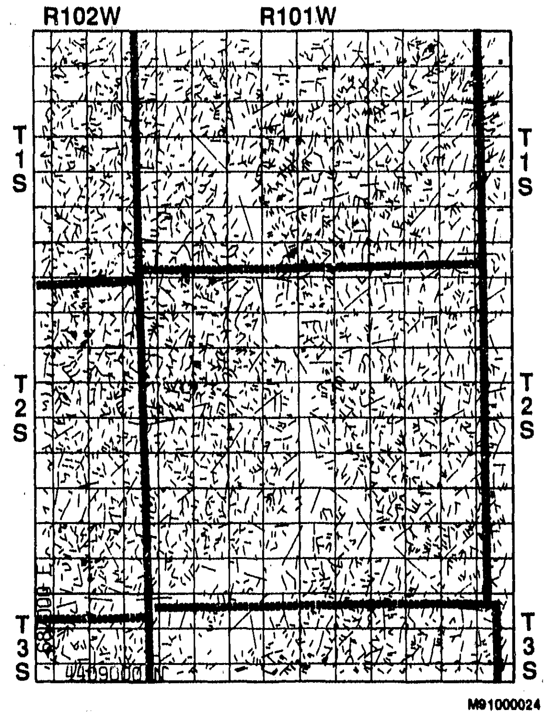

Figure 6. Map Showing Vectors Determined by Computer From Satellite Topographic Data (Digital Elevation Model) and Used in Co-Planar Lineament Analysis

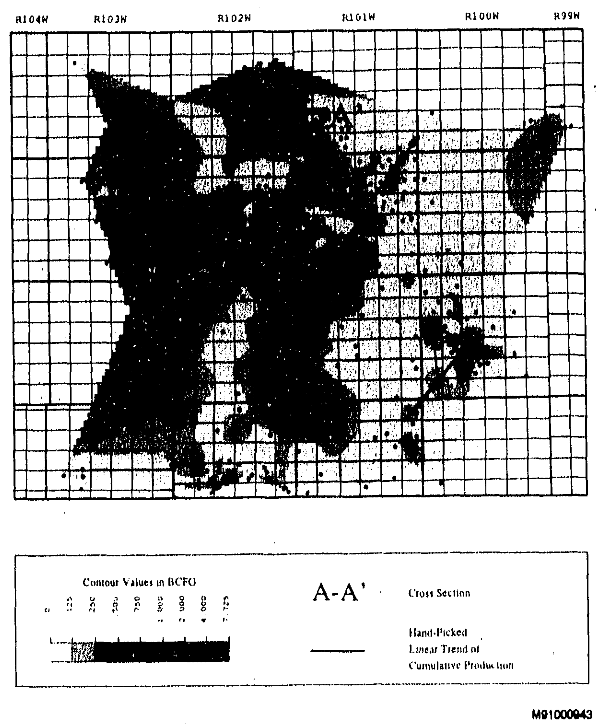

Figure 7. Contour Map of Total Cumulative Production From the Mancos B Formation

shown in Figure 3. All of the secondary planes, which are secondary because they don't have as great a degree of certainty as do the dominant planes since they are identified using fewer vectors, are shown in Figure 4. A rose diagram showing strikes of all planes determined by the analysis is displayed in Figure 5. Figures 3 through 5 show that the dominant strike direction of the planes is approximately north-south. Figure 4 shows that the orientations of secondary planes, of which there are enough to yield only five plane sets compared to 19 dominant plane sets, are northeast-southwest and northwest-southeast. Lineament Number 1 in Figures 3 and 4 appears to be the same, so the total number of plane sets from the analysis is 23.

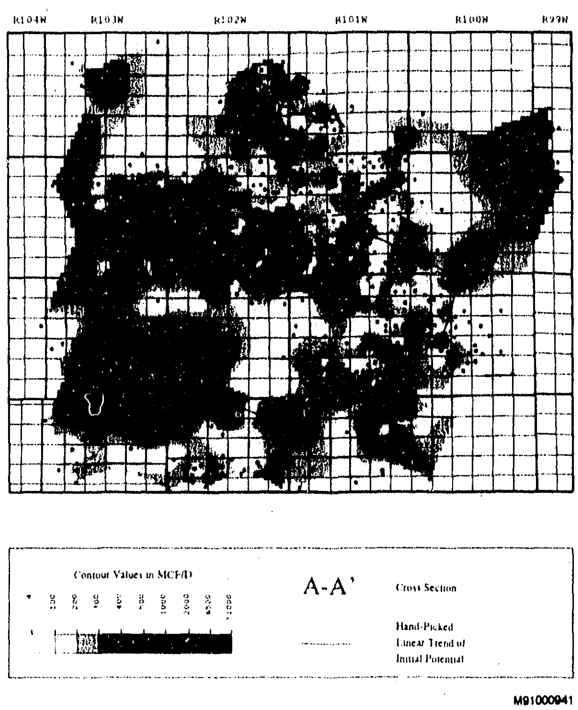

Figure 8. Contour Map of Initial Potential for Wells Completed in the Mancos B Formation

CO-PLANAR LINEAMENTS COMPARED WITH OTHER DATA

Comparison With Geologic Features and Linear Production Trends

Most co-planar lineaments failed to correlate with either a mapped geological feature such as a fault or with a linear trend on a contour map of cumulative production or initial potential. Unfortunately, those co-planar lineaments that showed the most correlation with geologic features or with linear trends on contour maps of production were those based on secondary plane sets determined with the fewest vectors. (Therefore, they had the least certainty.) The results of this portion of the study are presented in Tables 1 and 2.

The fact that co-planar lineaments don't have much value in predicting better areas of gas production, (i.e., those areas with better permeability) is similar to the findings of Klem and Mavor (1990). They evaluated photogeology, topography, and surface structural trends in the San Juan Basin in order to try to quantitatively predict permeability in the Fruitland coals in advance of drilling. They concluded that oriented core data were necessary to determine which surface lineaments and drainage pattern trends correspond to face cleat, butt cleat, and other fracture orientations.

The locations of co-planar lineaments in Figures 3 and 4 were first compared with faults locations on the geologic map in Figure 2. Twenty-three lineaments were detected with the co-planar lineament analysis. Figure 3 shows 19 lineaments, and the plane sets in Figure 4 would yield five more lineaments.

Table 1. Summary of Co-Planar Lineament Locations Compared to Locations of Other Features

Feature	Number of Lineaments With Same Location as Feature	Lineaments Number Having Same Location	Percent of Lineaments Having Same Location as Feature
	Surface Faults		
Tweto (1979), Figure 2	3	1, 2, 3	13
Petroleum Information	2	2, 3	9
	Linear Production Trends		
Computer-Drawn Maps: Cumulative Production, Figure 7	3	2, 3, 6	13
Initial Potential, Figure 8	3	3, 4, 5	13
Hand-Drawn Maps: Cumulative Production	3	2, 3, 6	13
Initial Potential	4	1, 5, 7, 8	17

[1] Proprietary information.

However, lineament Number 1 in both figures appears to be a duplicate; therefore, the total number of lineaments is 23. Of these 23 lineaments, only three (13%), or Numbers 1, 2, and 3 on Figure 4, roughly correspond to faults mapped by Tweto (1979) in Figure 2. Tweto mapped 11 faults in the area of the co-planar lineament study. Of these same 23 lineaments, only two (9%), Numbers 2 and 3 on Figure 4, correspond to faults mapped on a copyrighted, proprietary map made from air photos. Those co-planar lineaments that do show some correlation with the faults mapped by Tweto and on the proprietary map are those mapped on Figure 4, a map of secondary planes. J. R. Eliason (1990, Geologic Analysis and Consulting Services, Personal Communication) feels that these secondary planes are not as certain as the dominant planes determined with more vectors. Also, the co-planar features that do show some correlation are those that are 45° from the dominant north-south trend of the co-planar lineaments. A summary of these data is presented in Table 1.

Assuming linear trends on contoured production maps are caused by fracturing, the orientations and locations of the linear trends should be parallel to the orientations, and near the locations of, those fractures in the reservoir that are most effective in delivering gas to producing gas wells. The co-planar lineaments on Figures 3 and 4, were compared with the linear trends noted on the computer-contoured map (Figure 7) of cumulative total production through the end of 1988. Once again, three lineaments (13% of total), Numbers 2, 3, and 6 on Figures 3 and 4, corresponded to linear trends in cumulative production; Numbers 2 and 3 were from secondary plane sets. When the co-planar lineaments were compared with the linear trends on the computer-contoured map of initial potential (Figure 8),

Table 2. Summary of Orientations of Co-Planar Lineaments, Surface Measured Joints and Faults, and Linear Trends on Production Maps

Feature	Dominant Orientation
<u>Co-Planar Lineaments</u> (Figures 3 Through 6)	Mostly N-S, to slightly E or W of N-S; weakly defined ones trend N42 to 50E, and N60W.
<u>Surface Faults</u>	
Tweto (1979) Figures 2, 9A	N45 to 60E
Petroleum Information[1] Figure 9B	N30 to 60E, most N45 to 60E
<u>Joint Studies</u>	
Knutson (1977) Figure 10, Table 3	Data closest to co-planar study: N45 to 50W - major set, N45 to 55W - secondary set, N45 to 55E - conjugate to major set, N-S - conjugate to secondary set, N25W - third set.
Grout and Verbeek (1985)	Data is from Piceance Basin to east: Set F1 - NNE, Set F2 - WNW, Set F3 - ENE, Set F4 - NNE
<u>Lineaments From Air Photos</u>	
Kelley and Clinton (1960) Figure 11	Data is from southern portion of arch: N26 to 53E, N40 to 77W
<u>Linear Production Trends</u>	
Computer-Drawn Maps	
Cumulative production Figures 7, 12C	Almost random; most are: N30 to 45E, N45 to 60W, N0 to N15W, N60 to 75E
First Year's Production Figure 12B	N60 to 75W, N45 to 75E
Initial Potential Figures 8, 12A	N15 to 60W
Hand-Drawn Maps	
Cumulative Production Figure 13A	Almost random; most are: N15 to 75E, N75 to 90W, N30 to 45W
Initial Potential Figure 13B	N30 to 60E

[1] Proprietary information.

Table 3. Average Orientations of Joint Measurements on Douglas Creek Arch (from Knutson 1977)

Station No.	Location (Approximate)	Major Set	Conjugate To Major Set	Secondary Set	Conjugate to Secondary Set	Other Set
9E	6-1S-101W	N55W	N55E	E-W	N-S	N25W
9W	8-1N-102W	N45W	N45E	E-W	N-S	
18	8-7S-104W	N35W	N85W	N60W	N5E	
19	6-7S-102W	N15W	N60E	M40W	N20E	
20	36 7S-102W	N25W	N75E	N60W	N45E	

again three lineaments (13% of total) corresponded approximately with linear trends of production; these three lineaments are Numbers 3 and 4 on Figure 4 and Number 5 on Figure 3, with Number 1 on Figure 7 being close to one of the linear trends of initial potential.

The co-planar lineaments were compared to linear trends on a hand-contoured map of cumulative production (not included in this summary). Thirteen percent of the lineaments on Figures 3 and 4 corresponded approximately to linear trends on this map. When lineaments in Figures 3 and 4 were compared to linear trends on a hand-contoured map of initial potential (not included in this summary), 17% of the lineaments corresponded to linear trends on the contoured production map. Once more, the majority of co-planar lineaments that corresponded to linear production trends were those that are the less well-defined ones of Figure 4.

<u>Comparison With Orientations of Surface-Measured Linear Geologic Features</u>

The dominant north-south trend of the lineaments detected by co-planar lineament analysis (Figures 3 through 5) was quite different than trends of joints, faults, and topographical alignments mapped at the Earth's surface on the Douglas Creek Arch by other workers (Knutson 1977; Kelley and Clinton 1960; Tweto 1979). Table 2 is a summary of the data discussed in this section.

The state geologic map of Colorado (Tweto 1979) (a portion shown in Figure 2) shows many predominantly northeast-southwest trending normal faults; the data are plotted on a rose diagram in Figure 9A. The air photo interpretation done by a private company also shows faults and topographic alignments with a dominant northeast-southwest trend; the trends of these data are

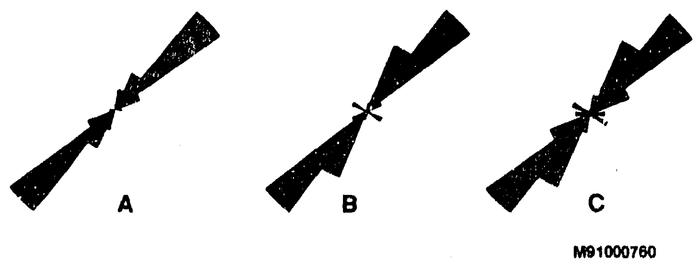

Figure 9. Rose Diagrams Showing Distribution of Strikes of Faults on Colorado State Geological Map (9A), Strikes of Faults and Drainage Alignments from Air Photo Interpretation (9B), and Trends of All Features Plotted in First Two Diagrams (9C)

plotted in Figure 9B. The strikes of all features on each of these maps are shown in Figure 9C. The data plotted in the rose diagrams were taken from T1S to T4S, R100W to R104W, an area that is slightly larger than that used in the co-planar lineament analysis. (See Figure 6.)

Table 3 and Figure 10 present data collected by Knutson (1977) on the Douglas Creek Arch. Some of the data were collected slightly north, and the remainder were collected about 30 miles south, of the co-planar lineament study. An examination of these data show that the major joint sets measured by Knutson (1977) at Stations 9E and 9W, which are the stations closest to the co-planar lineament study, trend N45W to N55W. The strike of the secondary set at each station is east-west. A weakly expressed north-south trending joint set is parallel to the dominant trend of the co-planar lineaments; Knutson considered this set to be a conjugate of the secondary set. The data collected at Stations 18, 19, and 20, which are about 30 miles south of the co-planar lineament study, show both the major and secondary sets to be oriented in a northwest-southeast direction. The orientation of the secondary set is only 25° in a counterclockwise direction from the major set, which ranges in orientation from N15W to N35W. Once again, the only joint set that is approximately north-south is conjugate to the secondary set, measured at Station 18 as having an orientation of N5E.

Although they have not studied joints on the Douglas Creek Arch, Grout and Verbeek (1985) studied the fracture patterns at several surface exposures in the Piceance Basin, which lies immediately east of the Douglas Creek Arch. They found four fracture trends in the basin: F1, which is oriented north-northwest; F2, which is oriented west-northwest; F3,

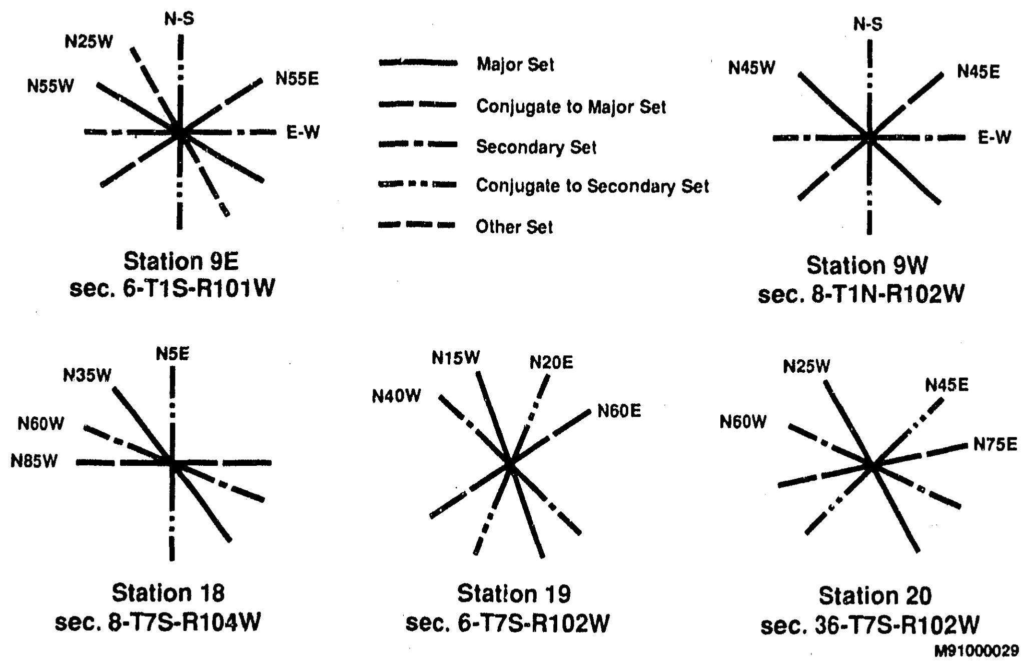

Figure 10. Directions of Joints Measured on the Douglas Creek Arch
(Knutson 1977)

which is oriented east-northeast; and F4, which is oriented north-northeast. Their results are pertinent because of the notable lack of north-south oriented fractures that are so prevalent in the results from the co-planar lineament analysis (Figures 3 through 5).

Kelley and Clinton (1960) mapped fracture patterns from air photos over most of the Colorado Plateau, including the southern portion of the Douglas Creek Arch (Figure 11). Their results correlate well with the surface measurements by Knutson (1977) in roughly the same area, and they also show a conspicuous lack of north-south oriented fractures. These workers found the most common trend for fractures to be oriented northeast-southwest, ranging from N26E to N50E. Slightly less common was a northwest-southeast trend of fractures, ranging in orientation from N40W to N77W. Since Kelley and Clinton obtained their data from air photos, it could be argued that the lack of north-south oriented fractures is caused by bias resulting from the direction of the sun's rays at the time the air photos were taken. This argument fails, however, because their data in Figure 11 compares favorably to those of Knutson (1977), especially Knutson's data measured on the southern portion of the Douglas Creek Arch at Stations 18, 19, and 20 (Table 3 and Figure 10).

<u>Comparison With Orientations of Linear Production Trends</u>

Not only is the dominant north-south trend of the co-planar lineaments (Figures 4 and 5) different than the orientations of previously mapped surface geological features, this trend is also different than the orientations of dominant linear trends in contour maps of cumulative production and initial potential (Figures 7 and 8). These data are also summarized in Table 2.

Figure 7 is a contour map of total cumulative production from the Mancos B Formation. The data were supplied by Dwight's Energydata, Inc., and are cumulative through the end of 1988. The data were contoured by the METC VAX computer using a bi-cubic spline contouring algorithm. Linear trends on Figure 7 were identified, and a rose diagram of these linear trends is presented in Figure 12C. There is an almost random spread of the data when compared to the rose diagrams of co-planar lineaments (Figure 5). The most

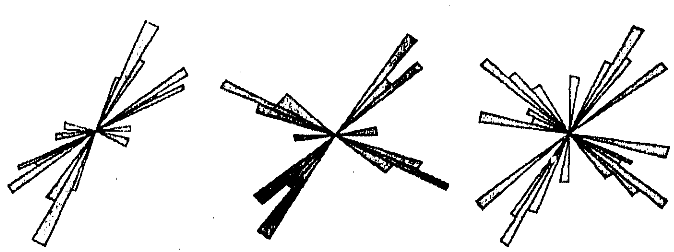

Figure 11. Regional Fracture Systems Mapped From Air Photos on Southern Portion of Douglas Creek Arch
(Kelley and Clinton 1960)

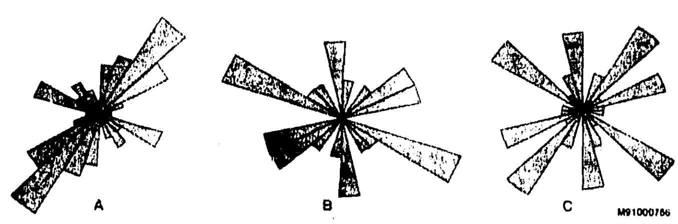

Figure 12. Rose Diagrams Showing Distribution of Hand-Picked Linear Features on Computer-Contoured Maps of Initial Potential (12A), First 12 Months of Production (12B), and Total Cumulative Production (12C), for Wells Producing From the Mancos B Formation

dominant orientations evident in Figure 12C are N30E to N45E and N45W to N60W; other slightly less prominent trends are N0 to N15W (approximately N-S) and N60E to N75E.

In a similar fashion, the cumulative production for the first 12 months of production for each well producing from the Mancos B Formation was plotted and contoured by computer. Linear trends in the data were again interpreted from the map and the results are displayed in the rose diagram in Figure 12B. The dominant trend is N60W to N75W.

Initial potential gas flow rates reported for all Mancos B Formation wells were obtained by computer from Petroleum Information's Well History Control System; the data were plotted and contoured by the same computer using the same algorithm as the cumulative maps discussed above. (See Figure 8.) Linear trends in the data were identified, and a rose diagram of these linear trends is displayed in Figure 12A. The dominant orientation is N30E to N45E.

In addition to marking linear trends on computer contoured maps of cumulative production and initial potential (Figures 7 and 8), linear trends were marked on hand-posted and hand-contoured maps with the same kinds of data. Rose diagrams showing the distribution of orientations of these data are presented in Figure 13. The rose diagram in Figure 13A shows orientations of linear trends on the hand-contoured map of cumulative production; the production data were supplied by Petroleum Information and are cumulative through the end of 1988. Figure 13A is similar to Figure 12C because there is an almost random distribution to the data; in Figure 13A, however, there is an even greater lack of north-south oriented production trends.

Figure 13B is a rose diagram showing the distribution of linear trends interpreted from the hand-posted and hand-contoured map of initial potential supplied on microfiche by Dwight's Energydata, Inc. The data show a pronounced northeasterly trend similar to Figure 12A, which displays trends on a computer-contoured map of the same type of data. Once again, a paucity of north-south trending lineaments is evident.

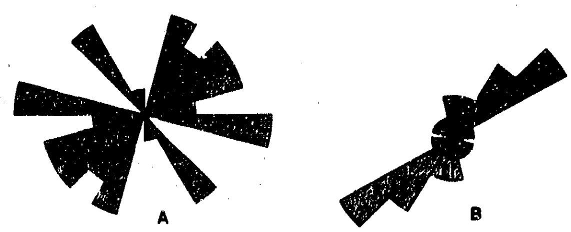

Figure 13. Distribution of Hand-Picked Linear Trends on Hand-Contoured Map of Cumulative Total Production (13A), and Initial Potential (13B), of the Mancos B Formation

DISCUSSION

Usefulness of Co-Planar Lineaments to Natural Gas Exploration and Development

The results of the co-planar lineament analysis show that its value to natural gas exploration on the Douglas Creek Arch is limited. Many lineaments are detected by the method (Figures 3 and 4), but only a small number show any correlation with gas production. Curiously, the less well-defined lineaments (Figure 4) correlated the best with gas production trends and mapped surface faults. Furthermore, the dominant trend of the lineaments (Figure 5) is quite different from the dominant orientations of linear trends on production maps (Figures 12 and 13).

The following are necessary for a natural gas reservoir to be economic: a structural or stratigraphic trap with an effective seal, a reservoir of sufficient porosity, a source rock that has generated gas, and a favorable hydrodynamic system that caused the gas to migrate to the trap. In the early days of oil and gas exploration, surface geology was used to identify possible structural traps. As more and more surface features became drilled, subsurface techniques were developed to measure directly or to infer what is today the *sine qua non* of a drillable gas prospect: a subsurface trap. These techniques include but are not limited to subsurface geological mapping with petrophysical well logs, reflection seismology, gravity data, and magnetic data.

Good permeability is a desired characteristic of a natural gas reservoir; however, if the above criteria of trap, reservoir, seal, source, and hydrodynamic environment are not met, the existence of permeability is academic. Permeability is one of the few characteristics of a gas reservoir that can be altered either by artificially fracturing a reservoir or by drilling a horizontal wellbore in order to encounter a greater number of permeable fractures. Since reservoir permeability is not as crucial to the success of a gas well, and since permeability can be altered, trying to identify areas of high reservoir permeability caused by fractures, whether or not they are indicated by surface lineaments, should not be the overriding concern when picking sites to drill natural gas wells.

For an explorationist in an unexplored area it would be difficult to know which of the many lineaments detected by the co-planar method would be the ones that would influence gas production the most. For an area in its development stage as is the Douglas Creek Arch, lineament analysis is not as effective or as low-risk as other techniques. In the development stage, well sites are often selected to fall along "sweet" spots or linear trends of better production. Sweet spots are determined by contour maps of cumulative production and initial potential. Drilling along a trend of better production doesn't, of course, guarantee success. Thus, subsurface geological maps, such as structure maps, and isopach maps are utilized in conjunction with production maps to recommend well sites.

A possible use of lineaments in development drilling would be in siting and determining the direction to drill a horizontal well that could take advantage of natural fractures in tight sandstone reservoirs. A lineament map might help to ascertain which of the many linear trends on a contour map of production, such as those on Figure 7, might have been caused by fracturing.

<u>Geologic Factors Other Than Fractures That Result In Straight Stream Segments</u>

One of the basic assumptions behind co-planar lineament analysis is that straight stream segments are caused only by joints. There are, however, other geological factors that result in straight stream segments.

In areas of folded strata, streams often develop a trellis drainage pattern. Long straight segments of streams flow parallel to outcrops of more easily erodible beds. The channel of a young stream often flows down the dip of the surface rocks. If the stream gradient is great enough, meanders will not form, and the course of the stream will be fairly straight and will closely parallel the dip direction of the surface rocks. Examples of this type of drainage are found in the Piceance Basin to the east of the Douglas Creek Arch; the causes of the drainage patterns are discussed by Whitney and Andrews (1983) and Whitney, Grout, and Verbeek (1984).

Extrapolating Surface Geological Data to Gas Reservoir Depth is Risky

Geological data measured at the Earth's surface, particularly information on joint orientation, can't always be extrapolated to the depth at which hydrocarbons are produced.

Grout and Verbeek (1985) studied natural fracturing at the DOE Multi-Well Experiment in the Piceance Basin. They concluded that "... surface and reservoir rocks contain no joint sets in common, and the study of one cannot be used to predict the occurrence of the other." Hancock and Engelder (1989) described a set of joints in the Devonian rocks of the Appalachian Plateau of New York. They noted that this joint set extends to a depth of only 0.5 km, and that its characteristics change markedly with increasing depth and differing lithologies. Nickelsen (1976) showed how joints in coals are different in orientation and spacing than joints present in the sandstones and shales with which the coals are interbedded.

Other geological structures should not be extrapolated to depth without careful study. Waechter and Johnson (1985) discussed a seismic line shot on the Douglas Creek Arch that shows basement faults dying out upward in the sedimentary cover. West and Lewis (1982), in a cross-section across a field in the Western Overthrust Belt, showed how the producing anticline and associated thrust fault are masked by an unconformity. Baars and Stevenson (1981), in a cross-section through a portion of the Paradox Basin, showed how a salt layer can separate flat-lying surface rocks from tilted fault blocks that produce oil. The Williston Basin has many examples of deep, oil producing structures that have no surface expression; Clement (1986) illustrated this concept with a cross-section over a portion of the Cedar Creek Anticline.

CONCLUSION

The co-planar lineament analysis method does not seem to be very useful to the exploration or development of natural gas from tight gas sand reservoirs on the Douglas Creek Arch. The location of most of the detected lineaments fails to correspond with either a mapped geological feature such as a fault or with a linear trend on a contour map of cumulative production or initial potential. Only 13 to 17% of the detected lineaments correspond to faults or to linear trends on contour maps of production data. Those lineaments that do show the most correspondence are those that are most weakly defined by the co-planar lineament analysis method. These data are summarized in Table 1.

The dominant trend of the co-planar lineaments is north-south. The dominant orientations of faults and joints in the area is northeast-southwest or northwest-southeast. The dominant orientations of linear trends on contour maps of cumulative production and initial production are highly variable, depending upon the data contoured and the person picking the linear trends. However, north-south oriented linear trends are noticeably absent in these data. These data are summarized in Table 2.

A significant correlation does not exist between co-planar lineaments and surface geological features such as joints and faults. This may be because the major premise of the co-planar lineament analysis (that topographic lows are joint-controlled) exaggerates the effect of joints upon drainage patterns. Many aspects of an area's geology, in addition to the joints, have an effect on a drainage pattern. Dendritic, trellis, radial, and consequent drainage patterns have streams with prominent linear segments, but these segments are primarily a result of a combination of bedding dip and strike and bedding erodibility.

It is not surprising to find a lack of correlation between lineaments mapped at the Earth's surface and natural gas production at depths greater than 1,000 to 1,500 feet. Lineaments, whatever their geologic origin, are direct manifestations of an area's <u>surface geology</u>. Natural gas entrapment, on the other hand, depends on the <u>subsurface geology</u> of an area.

Joints measured at the Earth's surface do not necessarily exist at depth. The rocks at depth are of a different age and lithology; they, therefore, have experienced a different stress history. Because mechanical properties of different rock lithologies can vary greatly, different types of rock may respond to stresses in different ways.

Any geological structure that exists at the surface cannot be extrapolated to the subsurface without supporting data or a sound theoretical basis. Faults, anticlines, and flat-lying bedding that are present on the surface may not extend for a large distance into the subsurface. Unconformities, plastic salt and shale layers, and thrust faults are examples of features that can mask subsurface geology from the surface.

The conclusion of this study is not that co-planar lineament analysis will never work in the search for unconventional gas. Rather it is that its application to natural gas exploration and development will not work everywhere. Areas where the technique would be best employed would probably be those where the reservoir is relatively shallow, the surface rocks and reservoir rocks are similar in age and lithology, and where the subsurface geology is relatively simple with no unconformities, thrust faults, or plastic layers such as salt or soft shale between the surface and gas reservoir. Additionally, it must be demonstrated that straight stream segments are indeed caused by joints in the surface rocks, not caused by some other geological phenomenon such as the strike of an easily eroded bed.

ACKNOWLEDGEMENTS

The opinions expressed are strictly those of the author, but the following people are to be thanked. Sue Pool and Bill Schuller of EG&G directed the METC VAX computer system to make the computer-contour maps and the rose diagrams. Tracy Weber, a summer ORAU student constructed maps and collected and posted the data from which some of them were made. Ray Lopez and Mark Portman also performed short-turnaround data gathering. Insight was gained from discussions with and comments by Keith Westhusing, Mark Evans, Steve Krehbiel, Chuck Spencer, and Rod Geisprecht. Mary Guide read a draft of the paper and suggested improvements.

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Extrapolation of MWX Data Into the Piceance Basin, Colorado

CONTRACT INFORMATION

Contract Number DE-AC21-88MC24120

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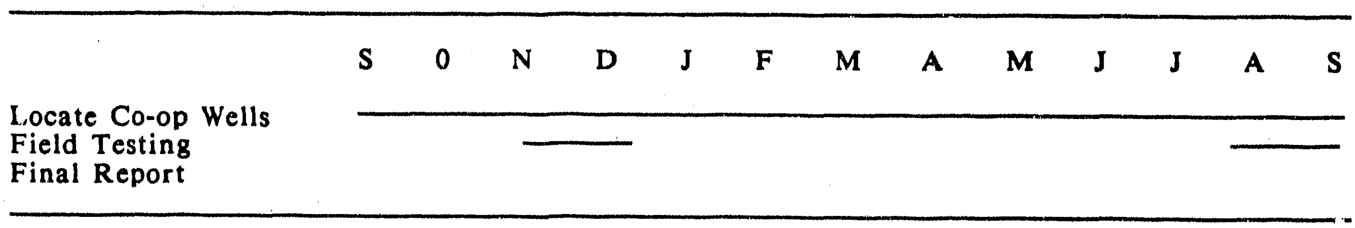
Period of Performance April 1, 1988 to November 29, 1991

SCHEDULE and MILESTONES

FY90 Program Schedule



OBJECTIVES

The principal objectives of this investigation are to:

- advance the technology developed at MWX into other areas of the Piceance Basin and verify the extrapolation potential of the geological and engineering findings and techniques;
- reliably identify and characterize potential areas for Mesaverde gas resource development; and
- develop an optimal methodology for developing this resource.

The ultimate goal of this investigation is to transfer this technology, in whole or in part, to the industry operators (i.e., gas producers) who can implement the technology on a wide scale and significantly increase gas reserves.

BACKGROUND INFORMATION

The Piceance Basin of western Colorado contains a major potential natural gas resource in the Mesaverde blanket and lenticular low permeability gas sands. The basin has been a pilot study area for government-sponsored tight gas sands research for over 20 years. This work culminated in the Multiwell Experiment, a field laboratory consisting of three closely-spaced wells, designed by the Department of Energy to study the reservoir and production characteristics of the low permeability Mesaverde sands near Rifle, Colorado.

PROJECT DESCRIPTION

A critical comparison is being undertaken of the geologic, production, and reservoir characteristics of the existing Mesaverde producing areas in the basin with those same characteristics at the Multiwell (MWX) site near Rifle, Colorado. In Phase I of this investigation a series of reservoir parameter maps from existing production were made. These maps include gross interval and net sand thickness maps, permeability thickness (Kh) maps, geothermal map, and ultimate production maps. Stimulation techniques were reviewed to determine the most effective stimulation technique currently used in the Mesaverde. The southern part of the Piceance Basin was partitioned into three areas of different characteristics as shown in Figure 1. The results of the Phase I investigation are reported in Myal and others, 1989.

Phase II of the investigation is underway and consists of field technology verification tests undertaken in the partitioned areas through cooperative projects with industry. These tests include oriented coring, logging, and pressure transient testing with extensive analysis. Of primary interest in these tests is the nature of natural fractures, their distribution, orientation with respect to stresses, and their significance to production.

RESULTS

Log Interpretation of Gas and Water Distribution

The gas and water distribution in the Mesaverde section was studied in detail for 34 wells in the Piceance Basin in Phase I of this investigation. This work serves as the basis for defining regional basin trends in gas and water distribution. This distribution is of particular importance in evaluating the nature of Piceance Basin coal bed gas production.

Figure 2 is a structural schematic of analyzed wells that crosses the central Piceance Basin generally from west to east. This section is centered on the Rulison Field and shows the position of the MWX. The schematic shows the tops of the marine, paludal and fluvial Mesaverde intervals.

A "top of gas" is shown on the schematic. This top is the uppermost sandstone which is interpreted to be at irreducible water saturation. Above this top, there is typically a series of sandstones that have some gas content; however, they are not at irreducible water saturation. The top of gas roughly parallels stratigraphy and structure across the major downdip portion of the section. On the updip margins of the basin, the top of gas cuts across stratigraphy. Generally, for a given stratigraphic interval, the gas lies downdip of water. The water updip phenomenon is characteristic of tight gas sand basins and relates to the gas trapping mechanism (Masters, 1979; Brown and others, 1986).

In this study we refer to a partially gas saturated section where water saturation is greater than irreducible as a "transition zone". This transition is between 100 percent water saturation and irreducible water saturation. This zone is typically 400 to 500 ft thick. The transition zone in this context could be called a zone of gas entrapment. There is a complete gradation from no gas entrapment to irreducible water saturation.

A conceptual model for the Mesaverde gas and water distribution involving the basin-centered gas trap is shown in Figure 3. From the model several conclusions of interest to operators can be made:

1. In the central section of the basin, at depth, all reservoir rocks will be gas saturated (except the Rollins sandstone). This includes the coals of the paludal interval such as the Cameo and other coals. The sandstone and coal reservoirs contain water around the basin periphery only. Coals in the central part of the basin do not have to be dewatered. The Piceance Basin coal play is therefore unlike that of the San Juan Basin in that the coals here are deeper and gas saturated in large portions of the basis.

2. In the central part of the southern half of the basin, at sufficient depth and at any location, chances are good that sands and coals will be penetrated. Those rocks will be gas saturated. Production will be enhanced if natural fractures are encountered by the wellbore or stimulation and are not damaged by fluids.

Field Verification Test-Central Basin.

In Phase II of this investigation two Mesaverde wells of opportunity have been undertaken. The first was with Barrett Resources in the Central Basin partitioned area (Figure 1). Sandstones of the fluvial interval were examined in the Grand Valley Field in the Barrett Resources MV 8-4 well of Sec. 4, T7S, R96W, Garfield County, Colorado. Services performed in the well for this study included taking 109 ft of partially oriented core, core analysis, TITEGAS log analysis, Formation MicroScanner (FMS) log analysis of fractures and borehole ellipticity, and a pressure transient test utilizing perforation under high nitrogen pressure differential toward the formation.

Fractures and Stresses. In the Barrett core only three short, mineral-filled natural fractures were found. Only one near vertical natural fracture striking N78°W could be oriented. No natural fractures were identified on the FMS log. Numerous drilling-induced fractures were found both in core and on the FMS log. Strikes of the induced fractures measured in core and those interpreted from the FMS log are shown in Figure 4.

Because the FMS log contains a dual oriented caliper, an analysis of borehole ellipticity could be done on the Barrett well. An elliptical wellbore is defined as one in which one calliper reads larger than the other due to borehole sidewall breakouts. The ellipticity analysis of the Barrett MV 8-4 well is shown in Figure 5A. Ninety elliptical zones were found in 2,000 ft of wellbore with a mean direction of the wider caliper of N2°W $\pm$7 .

Studies of wellbore breakouts by several researchers, such as Blumling and others (1983), have shown that breakouts (elliptical wellbore long axis) parallel the minimum horizontal principal stress. Stress-induced ellipticity should be oriented perpendicular to extension fractures developed under the same stress regime. Inferred fracture orientations from the borehole ellipticity are shown in Figure 5B. A comparison of Figures 4 and 5A infers a consistent orientation of the maximum horizontal stress to be between N70°E and N90°E. This stress orientation is different from that reported in the MWX fluvial interval by Teufel and others (1984) and suggests a counter clockwise difference of about 10 degrees from that at MWX.

Pressure Transient Test. A pressure buildup test of a 14 ft thick fluvial sandstone in the Barrett well has been completed and analyzed. The Horner plot and log-log plots of the pressure buildup and a derivative curve are shown in Figures 6 and 7, respectively. Initially, an attempt was made to analyze the buildup test using conventional analytical solutions to pressure buildup curve shape. However, due to the lack of a clear straight line region of the curve and the ever increasing slope, it was not possible to determine the reservoir characteristics analytically. Therefore, the computer simulation approach was necessary to analyze the buildup. A single-phase three-dimensional simulator was used to model the bottomhole pressure response to acquire a reasonable match in both the Horner coordinates and the log-log plot.

The shape of the buildup curves strongly indicates reservoir heterogeneities resulted from boundary effects and, as the slope of the Horner plot is constantly increasing, more than one boundary may be expected. Many different reservoir geometries were examined with the well located at varied distances from the boundaries. The final match was achieved by locating the well at the center line of a 32-ft wide channel with infinite length.

Because there was not data to substantiate vertical layering that can affect gas flow behavior of the MV 8-4 well, a single-layer system was used in this analysis. A zone extending 6 ft from the wellbore with an increased permeability of 10 md was used in the model to represent reservoir stimulation as a result of high pressure nitrogen perforation/breakdown.

The model predicted pressure behavior and the shape of the curves are very similar to the actual data, indicating the channel geometry is a possible shape of the reservoir. Other reservoir heterogeneities such as the presence of natural fractures or reservoir layering can probably produce similar pressure response in a buildup test, however, there was not enough information to support a computer model analysis. No identifiable natural fractures were interpreted on the FMS log in the test interval. It should also be noted that the term "channel" does not necessarily mean the reservoir is actually a river channel, although the test interval was in the Mesaverde fluvial section. It only indicates the pressure buildup process can be reproduced by using this bar-shaped reservoir with two parallel boundaries 32 ft apart.

Field Verification Test- Southwest Flank. The second cooperative well is with Fuel Resources Development Company (Fuelco) in the Southwest Flank partitioned area (Figure 1) in Sec. 22,T10S, R94W, Mesa County, Colorado. Phase I of this investigation showed that the eastern side of the Plateau Field will have higher ultimate production from the marine Cozzette and Corcoran than the rest of the field (see Myal and others, 1989, Figure 29). The Fuelco well is an offset to the better production, so the objective of the cooperative well is to verify the cause of the better production. The investigation consists of 120 ft of oriented coring on the Cozzette and Corcoran, core analysis, TITEGAS log analysis, analysis of borehole televiewer and FMS logs, and a pressure transient test. Drilling, coring,and logging have been completed and data is now being analyzed. The pressure transient test is presently being conducted.

Several open natural fractures, as well as several coring induced fractures, were recovered in each core and identified on the televiewer and FMS images. The core was only partially orientable but an attempt is being made to orient the remainder with the fracture logs.

FUTURE WORK

Cooperative agreements for more field verification tests are being sought with industry operators in the partitioned areas of southern Piceance Basin. Negotiations are underway with Mobil for testing a thin coal seam recently cored on the boundary between the Central Basin and Southeast Uplift areas. In future work the following observations by operators will be investigated:

- The thin coals are more productive than thick coals.
- Thin coals have better developed cleat structure than thick coals and may be more permeable.
- Thinner coals are commonly higher rank than underlying thick coals.

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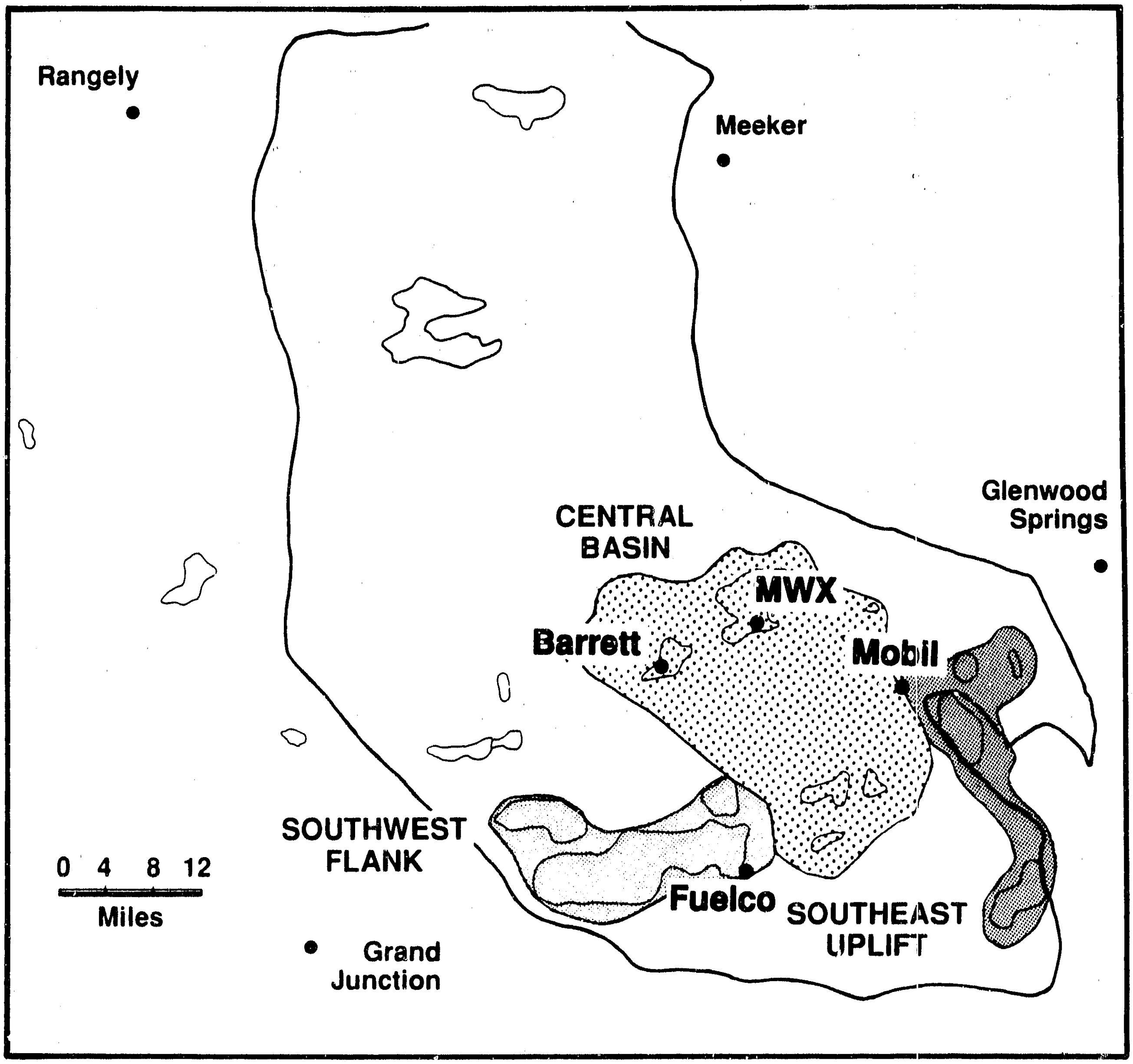

Figure 1. Partitioned Areas with Well Locations

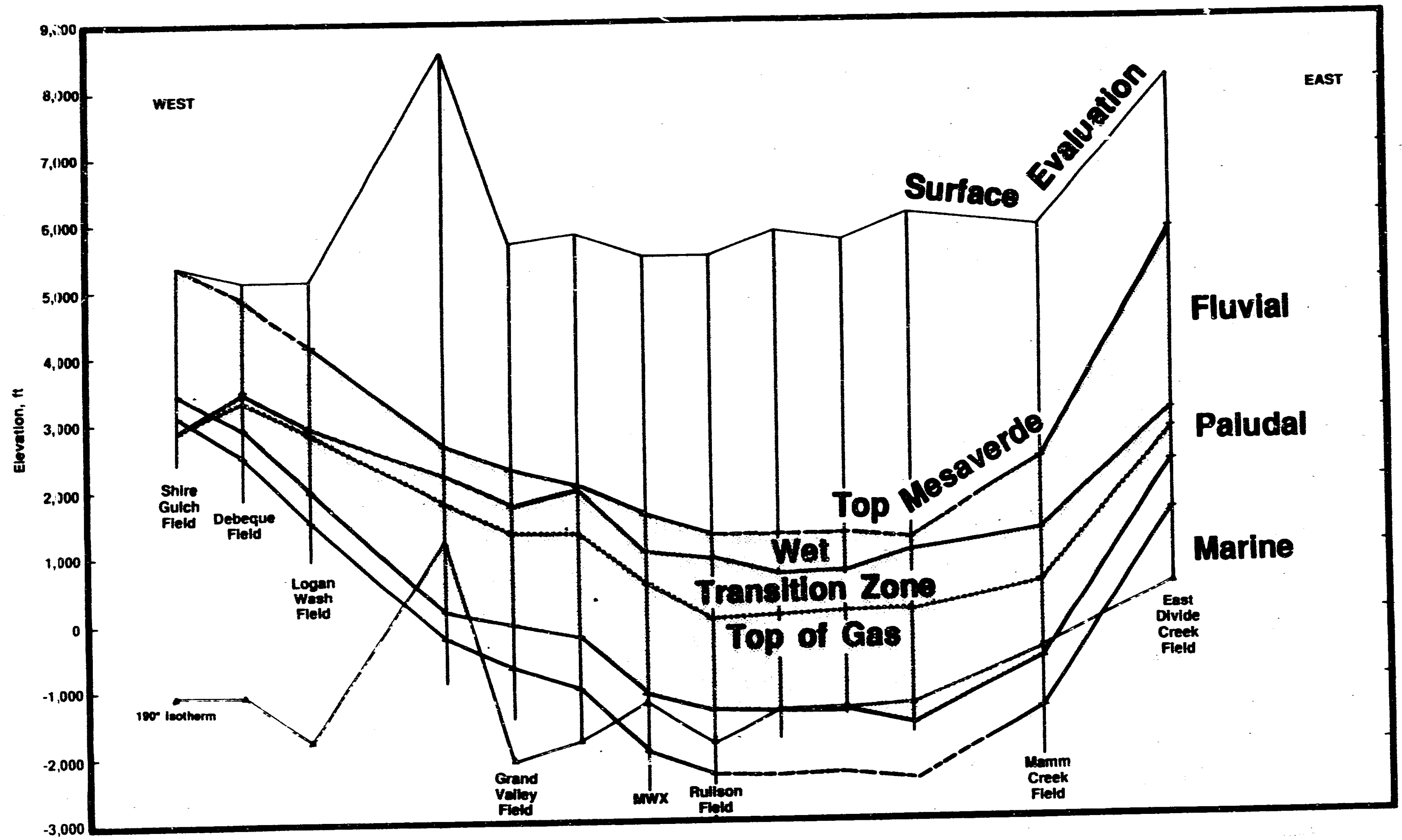

Figure 2. Cross Section with Wells

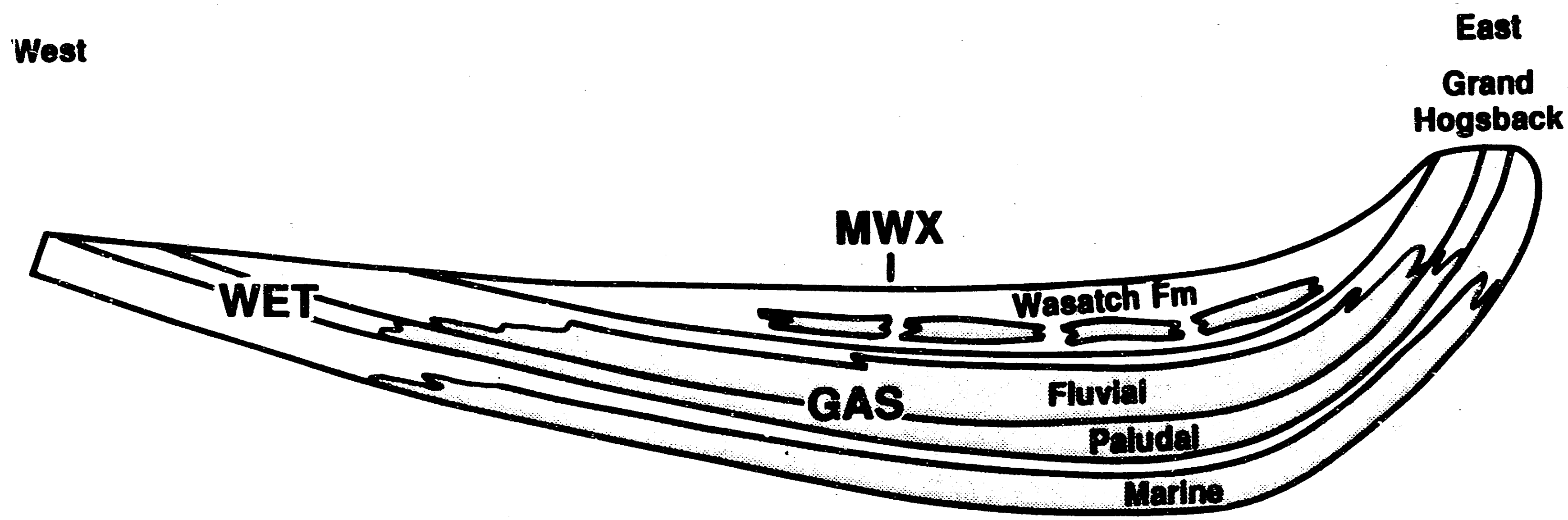

Figure 3. Conceptual Model of Basin Centered Gas

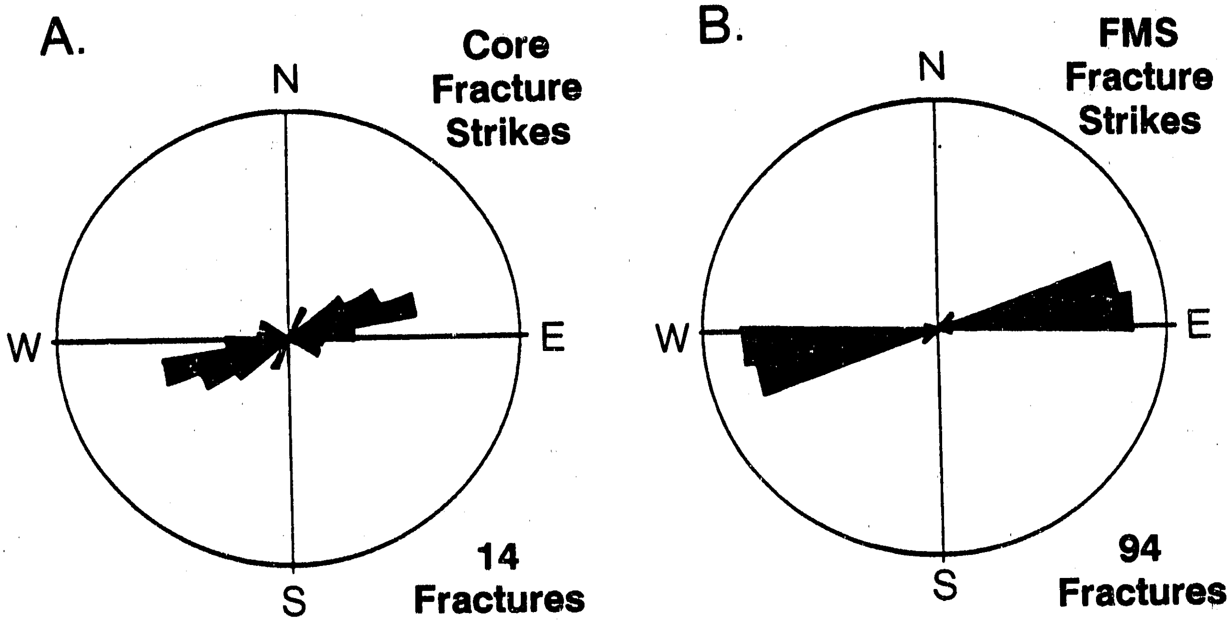

Figure 4. Core Fracture Strikes, FMS Fracture Strike

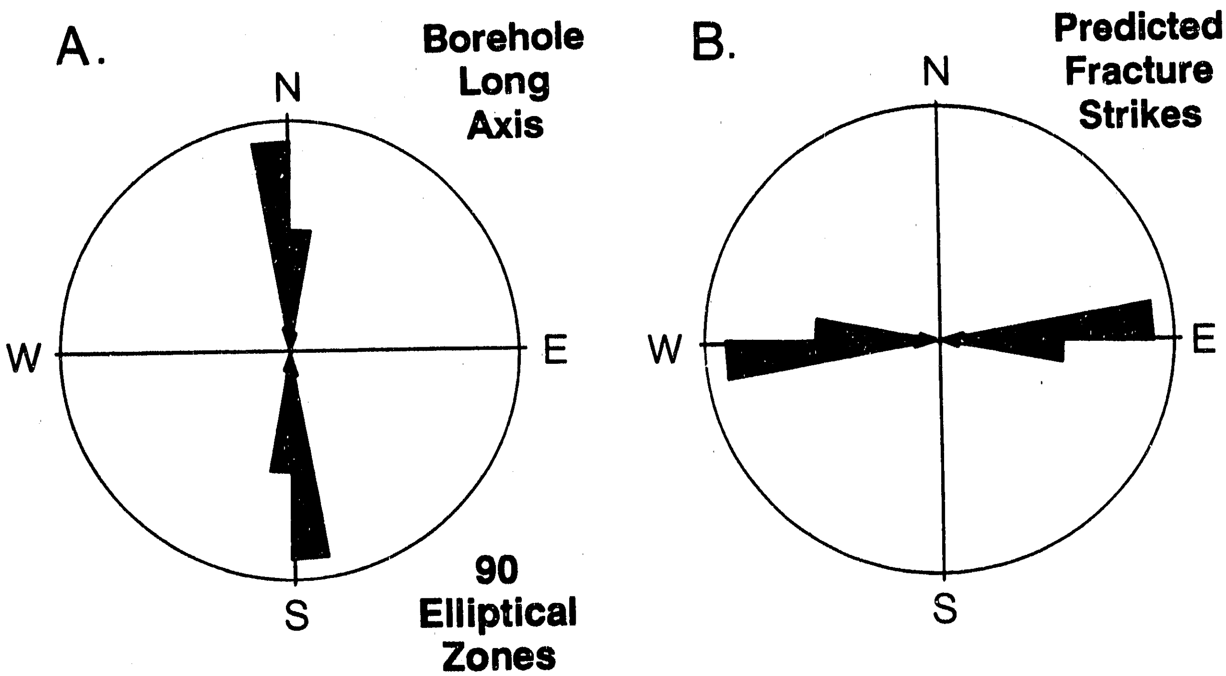

Figure 5. Borehole Ellipticity, Predicted Fracture Strikes

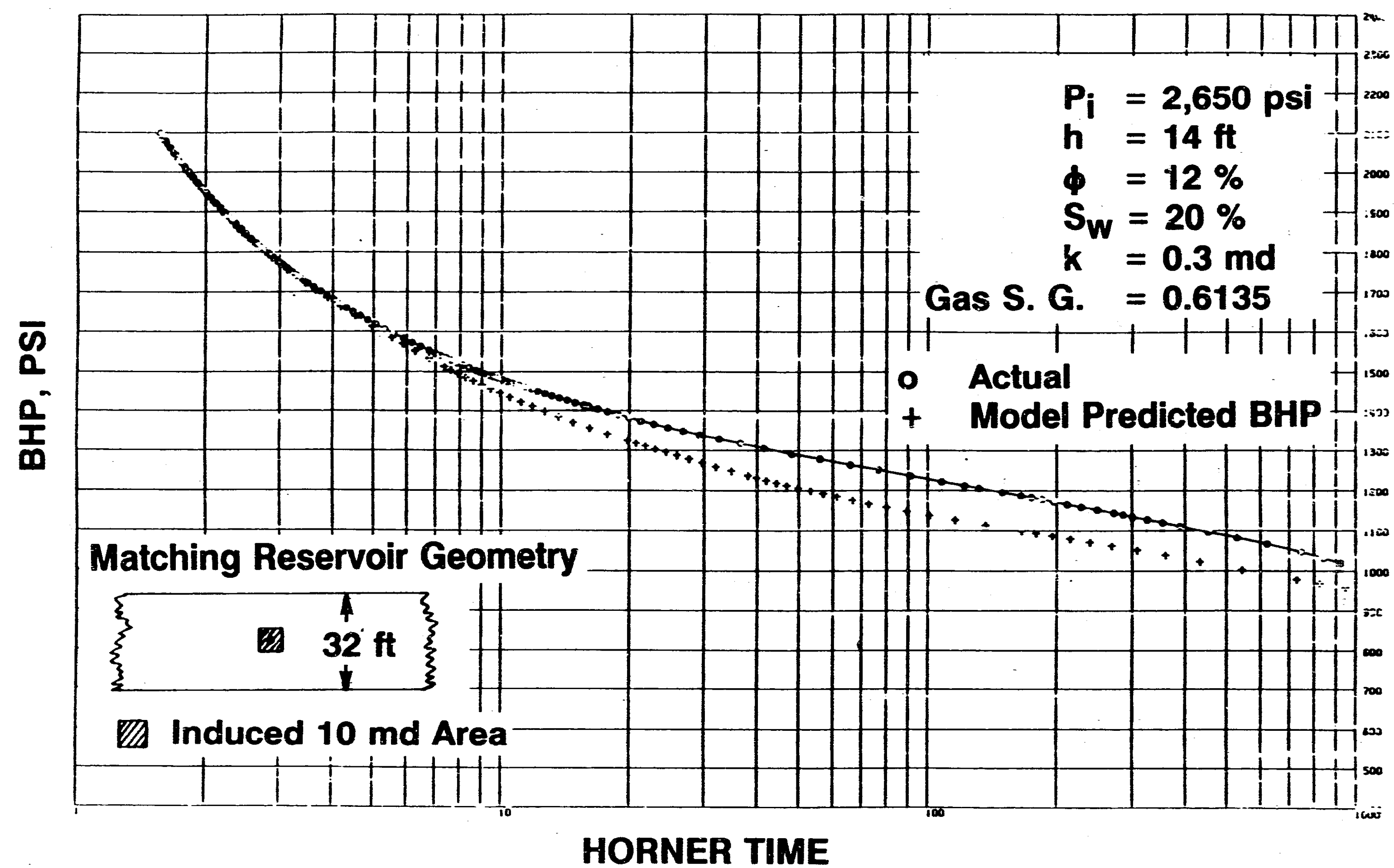

Figure 6. Horner Plot of Barrett MV8-4 Pressure Buildup

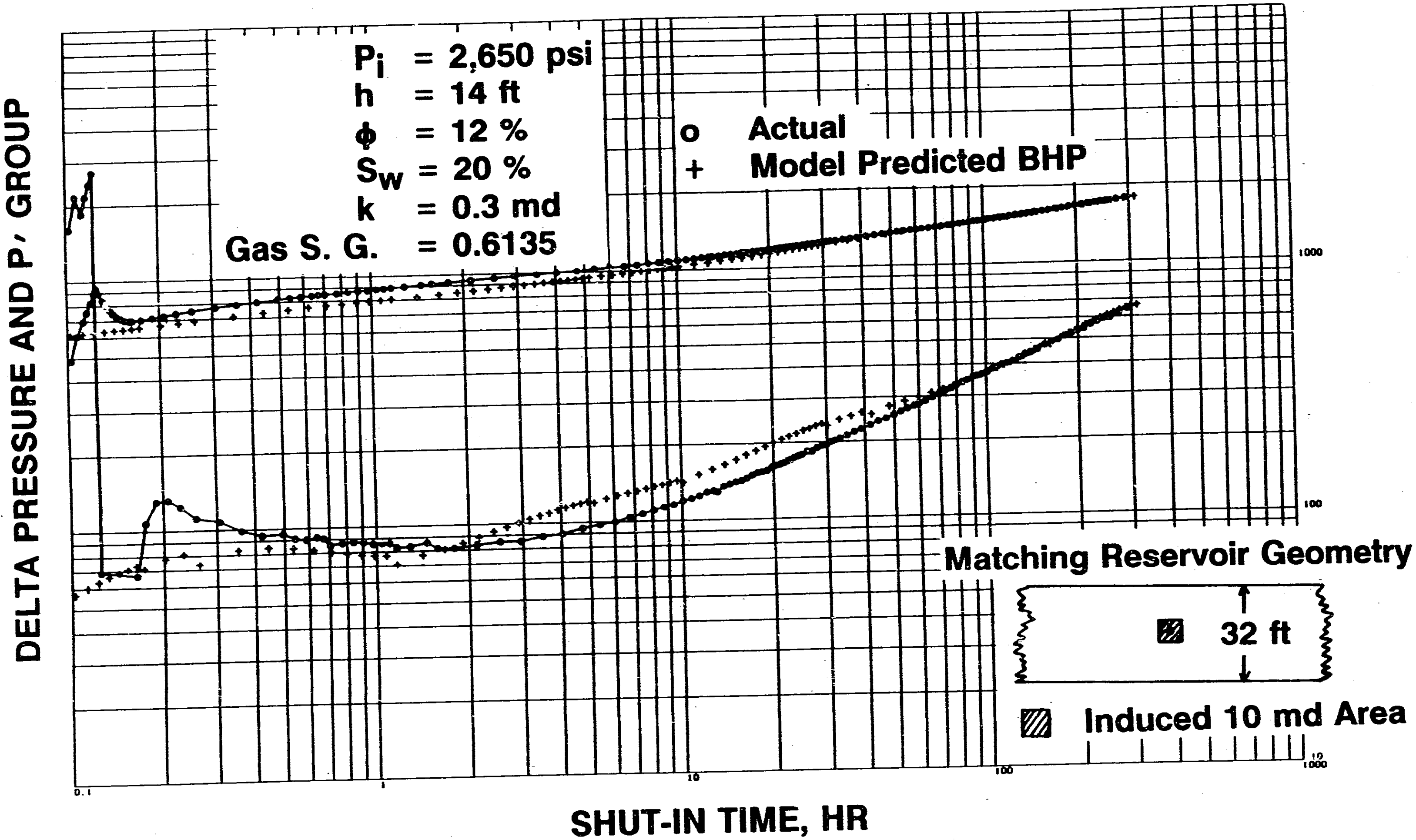

Figure 7. Log-Log Plot of Barrett MV8-4 Pressure Buildup

Slant Hole Completion Test
Mesaverde Group, Piceance Basin, Colorado

CONTRACT INFORMATION

Contract Number	DE-AC21-90MC26024
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Principal Investigators	F. Richard Myal Gerald C. Kukal Robin E. Hill
METC Project Manager	Karl-Heinz Frohne
Period of Performance	January 1, 1990 to September 8, 1990

Schedule and Milestones

FY90 Program Schedule

		S	0	N	D	J	F	M	A	M	J	J	A	S
Task 1	Site Access													
Task 2	Well Planning													
Task 3	Well Drilling													
Task 4	Disposition													

OBJECTIVES

The objective of the slant hole completion test, funded by the U.S. Department of Energy, is to evaluate directional drilling as an alternative development strategy for the tight, naturally fractured sands and coals in the Mesaverde Group in the Piceance Basin. This paper discusses the drilling, coring, logging and casing operations for the slant hole.

BACKGROUND INFORMATION

The Piceance Basin of western Colorado contains a major potential natural gas resource in the Mesaverde blanket and lenticular tight, naturally fractured sands and coals. The basin has been a pilot study area for government sponsored tight gas sand research for over 20 years. Early production experiments included both nuclear stimulations and massive hydraulic fracture treatments. This work culminated in the Multiwell Experiment, a field laboratory with three closely spaced wells designed by the and production characteristics of the low permeability, naturally fractured gas sands in the Mesaverde Group near Rifle, Colorado.

PROJECT DESCRIPTION

The surface location for the slant hole completion test is 700 ft south of the DOE Multiwell Experiment site in Section 34, T6S, R94W, Garfield County, Colorado. The hole was designed to intersect the paludal Mesaverde 3 and 4 sands and bounding coals at 60° beneath the Multiwell pad, and to proceed north to intersect the Cozzette at 88° and drill parallel to bedding for a distance of 500 ft. The well was positioned to drill normal to the regional fracture trend as identified in previous studies undertaken at the Multiwell Experiment. The slant hole completion test was spudded April 10, 1990 and reached 9,466 ft TMD in the Cozzette August 4, 1990.

A 12-1/4 in. hole was drilled through the Wasatch and 200 ft into the Mesaverde to a depth of 4,130 ft to isolate major caving and lost circulation zones. A 9-5/8 in. 36 lb/ft K55 intermediate casing string was run to 4,130 ft and cemented back to surface.

An 8-3/4 in. hole was then drilled vertically to the first KOP at 6,365 ft. Hole angle was then built in the 8-3/4 in. hole using a 6-3/4 in. diameter Mach I motor at a build rate of 8.7°/100 ft, to a hole angle of 59.3° at 7,305 ft MD. Conventional rotary coring operations were undertaken in the paludal Mesaverde between 7,305 and 7,581 ft MD. This included a 9 ft pressure core in the coal between 7,371 and 7,380 ft MD, co-funded by the Gas Research Institute, for a direct determination of coalbed methane content. Rotary drilling operations then proceeded at 60° from 7,581 to 8,667 ft in the Mancos shale, below the base of the Rollins sand. The combination of lost circulation in the Rollins and caving in overpressured coals and fractured siltstones at 7,350 to 7,400 ft MD necessitated running the 7 in. casing to isolate these intervals. The 7 in. 29 lb/ft N80 casing was run to 8,489 ft where it became stuck and was cemented in place with 770 sx cement. The 5 in. drillpipe and handling equipment was changed out to 3-1/2 in. equipment.

A 6 in. hole was then rotary drilled to the second KOP at 8,834 ft MD. The second build was drilled from 8,834 to 8,949 ft with 4-3/4 in. diameter, 19.4°/100 ft Mach I angle build motors. Inclination was built from 62.5° to 81.5° for an effective build rate of 15.3°/100 ft. The last 40 ft of the second build was drilled with a conventional rotary angle-build assembly due to extreme difficulty sliding the small tools in the high angle second build interval. The effective hole angle at the end of the second build was 85.1° at 8,990 ft MD. Conventional rotary coring was undertaken in the Cozzette between 8,990 and 9,108 ft MD. The hole was then rotary drilled to 9,466 ft TMD and the open hole section was successfully logged using drillpipe conveyed logging techniques. A 4-1/2 in., 13.5 lb/ft, N80 liner was run to 9,466 ft MD (top liner tieback at 8,200 ft MD) and cemented with 300 sx cement. Mechanical problems that developed following liner cementing operations resulted in a major washover operation and temporary suspension of activities on the well. Figure 1 illustrates the wellbore configuration while Figures 2 and 3 present the wellbore profile and plan views.

RESULTS

First Build

A gyroscopic survey run at 6,365 ft, the first kickoff point, determined the bottom hole location to be 65.83 ft east and 26.30 ft north of the surface location on an azimuth of N68°E. The eastward drift of the hole is attributed to intersecting and tracking a minor fault scarp initially intersected at 2,622 ft. The target inclination was 60.5° at an azimuth of N4°W. The entire curve was drilled with 8.7°/100 ft Mach I angle build motor assemblies. The first build interval was finished at 7,010 ft MD with an inclination of 53.2° on an azimuth of N4.3°W.

Tangent

The first tangent section was started with a steerable DTU Mach I motor assembly. This assembly drilled 295 ft to the first core point at 7,305 ft while increasing the hole angle to 59.3°. At this point, a wiper run was made with an 8-3/4 in. hole opener prior to initiating coring operations.

Pressure Core in Paludal Coal. Two 10 ft pressure cores were cut in siltstone and coal stringers between 7,305 and 7,324 ft. Following a reaming run to open the hole from 6-1/2 in.

to 8-3/4 in., 47 ft of conventional core was cut (in three runs) and the 10 ft coal seam at the top of the paludal 4 sand was located at 7,366 ft MD. Five feet of coal was cut with the conventional core barrel and packed in canisters for methane desorption measurements. A pressure core was taken in the 60° wellbore from 7,371 to 7,380 ft with 9 ft of coal recovered and full pressure at the surface. Subsequent desorption of the pressure core indicated a methane content of 765 SCF/ton, not corrected for ash content. Table 1 presents the results of coal desorption testing using samples from the conventional core and pressure core.

Conventional Core in Paludal Mesaverde. Conventional core was cut from 7,324 to 7,371 ft, and from 7,380 to 7,581 ft in the 60° inclined wellbore. The first two core runs, from 7,324 to 7,341 and from 7,341 to 7,358 ft, were prematurely terminated by core barrel jamming due to the highly fractured nature of the coals, siltstones, and shales encountered. The third core taken from 7,348 to 7,371 ft was terminated 5 ft into the coal to initiate pressure coring operations. The fourth core taken from 7,380 to 7,418 ft encountered 5 natural fractures and was terminated when the core barrel jammed in a minor coal. The fifth core taken between 7,418 and 7,478 ft encountered 9 natural fractures in 39 ft of fine to medium grained sandstone. The sixth core taken from 7,478 to 7,538 ft encountered 26 natural fractures in 29 ft of fine grained sandstone. The seventh core taken from 7,538 to 7,581 ft encountered 5 natural fractures in 24 ft of fine grained sandstone, 10 ft of mudstone, and 7 ft of coal. The coal recovered between 7,571 and 7,579 ft was loaded immediately into canisters for low pressure gas desorption. Core recovery included the coal above the paludal 4 sand, the paludal 4 and 3 sands, and the coal below the paludal 3 sand. Table 2 summarizes the fractures in the paludal core.

Fishing Operations. Drilling the tangent continued after coring operations with the 8-3/4 in. hole being drilled to 8,667 ft. Nine BHA's were employed in this interval including both rotary and steerable DTU motor assemblies. A fishing operation at 7,829 ft resulted from losing two cones from an F3HL bit while drilling with a steerable motor and MWD to raise hole angle. A second fishing operation at 8,270 ft resulted from losing one cone and two nose cones and bearings from a second F3HL bit while drilling with a steerable motor and an MWD to raise hole angle in the tangent section.

Hole Caving and Lost Circulation. Lost circulation into the Rollins sand penetrated at 8,199 ft caused the drillpipe to become differentially stuck while drilling at 8,270 ft. The overpressured coals and fractured siltstones above the Rollins then kicked, unloading gas into the wellbore causing the hole to cave. The drillpipe was worked loose and the Rollins was successfully treated with Flo-Chek to mitigate lost circulation. Drilling operations continued with much difficulty and frequent tight spots to 8,667 ft. On a short trip to insure the hole was clean, the drillpipe became stuck at 7,414 ft. Circulation with full returns was maintained even though the drillpipe could not be rotated or reciprocated. With the frequency of hole caving in the paludal coals and occurrence of stuck drillpipe steadily increasing, a decision was made to run and cement the 7 in. casing at 8,667 ft. Due to the threat of caving, no openhole logs were run in the 8-3/4 in. wellbore.

Set 7 In. Casing at the Base of the Rollins. One hundred ninety eight (198) joints of 7 in., 29 lb/ft N80 LT&C casing were run in the well to 8,489 ft, 290 ft below the top of the Rollins and into the Mancos shale. One hundred twelve centralizers were placed on 20 ft centers throughout the tangent and build sections of the hole. The hole was very tight between 7,287 and 8,489 ft where the casing stuck, 178 ft off bottom. The casing had to be worked and washed down through this interval. Full returns were experienced during washing and running the casing to 8,489 ft. The 7 in., 29 lb/ft N80 casing was cemented with 340 sx of AG 250 lead cement containing 10% blended Silica Lite, and 1% HR12 followed by 430 sx of AG 250 tail cement containing 35% silica flour, 10% blended Silica Lite, 0.7% Halad 413, 1.4% HR12, and 0.2% Super CBL. Full returns were experienced throughout the job. A cement bond log run five days after completion of cementing operations indicated the cement top at 6,405 ft, approximately 40 ft below the top of the first build, and 2,900 ft below the calculated cement top of 3,500 ft.

Slim Hole Drilling with 6 Inch Tools. Running the 7 in. casing at 8,489 ft, necessitated changing out the 5 in. drillpipe, 5 in. HWDP and handling equipment with 3-1/2 in. S135 drillpipe and handling equipment. The 4-3/4 in. Sperry Sun MWD was employed to determine hole inclination and azimuth. Following drillout of the shoe joint, a 6 in. PDC bit was used to drill the remainder of the tangent interval to the second kickoff point at 8,834 ft MD. The tangent interval was completed at a depth of 8,834 ft with a hole inclination of 62.5° on an azimuth of N4.3°W.

Second Build

The second kickoff point was determined using detailed structural mapping in conjunction with well to well correlations to recognizable stratigraphic markers. These stratigraphic markers, illustrated on Figure 4, include the paludal coals, Rollins sandstone, Mancos Tongue and a thin gamma ray marker 84 ft (TVD) into the Mancos Tongue. This was combined with MWD survey information to successfully project the expected depths of the markers. This procedure resulted in an accurate determination of the second kickoff point at 8,834 ft MD.

The second build interval was drilled with 19.4°/100 ft Mach I angle build motors using PDC and natural diamond bits. Nine fixed angle build assemblies were run between 8,834 and 8,949 ft, including one milling run at 8,894 ft MD. Penetration rates were very low while drilling the second build interval due to difficulty continuously sliding the 4-3/4 tools in the high angle hole. Inclination was built from 62.5° at 8,834 ft to 81.5° at 8,949 ft for an effective build rate of 15.3°/100 ft. A rotating angle build assembly was run at 8,949 ft to drill to the end of the second build in the Cozzette at 8,990 ft. The second build interval was completed at a depth of 8,990 ft in the upper Cozzette target interval with a hole inclination of 83.4° on an azimuth of N1.2°W.

Horizontal Section

Cozzette Core. A 6 in. diamond corehead and a 30 ft conventional core barrel, with brass wear pads at the mid-point position on the inner barrel to serve as stabilization, were used to cut 116 ft of core in the Cozzette interval. Since the Cozzette dips to the north at 1.7° and the wellbore azimuth is essentially due north, the wellbore penetrates the Cozzette at an effective angle of 85.1°. The eighth core taken from 8,990 to 9,020 ft recovered 30 ft of sandstone containing 5 natural fractures. The ninth core taken from 9,020 to 9,050 ft recovered 30 ft of sandstone with 12 natural fractures. The tenth core taken from 9,050 to 9,080 ft recovered 26 ft of sandstone containing 11 natural fractures. The eleventh core taken from 9,080 to 9,108 ft recovered 26-1/2 ft of sandstone containing 7 natural fractures. Gas entry during coring operations caused the drilling fluid to gas cut from 16.6 PPG to 16.4 PPG while cutting the last core. Thirty five (35) mineralized, open, natural fractures were observed in the 116 ft of core taken in the Cozzette. Table 2 summarizes the fractures in the Cozzette core.

Rotary Drilling the Cozzette Lateral. Following completion of coring operations at 9,108 ft, a rotary angle build assembly was run in the hole with a natural diamond bit. Numerous natural fractures were encountered drilling from 9,108 to 9,398 ft MD, the bottom of the upper Cozzette interval. Progressive penetration of fractures was indicated by loss of 16.6 PPG drilling fluid and sporadic increases of gas on the chromatograph while drilling. The hole was bottomed at 9,466 ft, approximately 68 ft into the siltstone below the base of the upper Cozzette interval.

Logging the Cozzette Lateral. Drillpipe conveyed openhole logging operations were conducted in the Cozzette. The sidedoor entry sub was attached after running 6,400 ft of drillpipe. The Dual Induction-SFL, Lithodensity-Compensated Neutron, Gamma Ray, and Caliper logs were run from 9,466 ft back to the base of the production casing at 8,489 ft. The Gamma Ray and Neutron log were run inside the 7 in. casing back to the cement top at 6,405 ft MD. The drillpipe conveyed logging operations were conducted in one run and were completed, without incident, in 22 hours.

Set 4-1/2 In. Liner at 9,466 Ft TMD. Twenty nine (29) joints of 4-1/2 in., 13.5 lb/ft N80 LT&C Range 3 liner and the tieback assembly were run on the 3-1/2 in. drillpipe to 9,466 ft. The top of the liner tie back sleeve was landed at 8,200 ft and the liner was centralized at 20 ft intervals throughout its length. The liner was cemented with 300 sx of premium AG 250 cement containing 35% silica flour, 0.7% Halad 413, 1.4% HR-12, 0.5% CFR-3, 0.3% Super CBL, and 1/4 lb/sk Flocele mixed at 17 lb/gal.

Following 12 hours WOC, a rerun 6 in. bit and a casing scraper were run in the well to 7,822 ft, approximately 400 ft above the liner tie back to clean out the expected 200 to 300 ft of fill.

At 400 ft above the liner tieback, heavy mud cut cement and practically straight cement was circulated from the hole. The drillpipe was worked until returns became too thick to pump. Attempts to reverse circulate down the casing-drillpipe annulus, and to pump straight water down the drillpipe to move the mud, proved unsuccessful. Pipe recovery operations were started immediately at 346 ft. September 5, 1990, when DOE issued the 90 Day Stop Work Order, pipe recovery operations were at 5,335 ft. Recovery to date included 166 joints of 3-1/2 in. drillpipe. One 2-1/4" by 42 ft chemical cutter tube, 81 joints of 3-1/2 in. drillpipe, one 6 in. casing scraper, one bit sub, and a 6 in. bit remain in the hole.

FUTURE WORK

Future work will include preparation of drilling prognosis and cost estimate to cut off and pull the 7 in. casing at 5,300 ft, and then drill a sidetrack parallel to the existing hole, 1,000 ft to the east.

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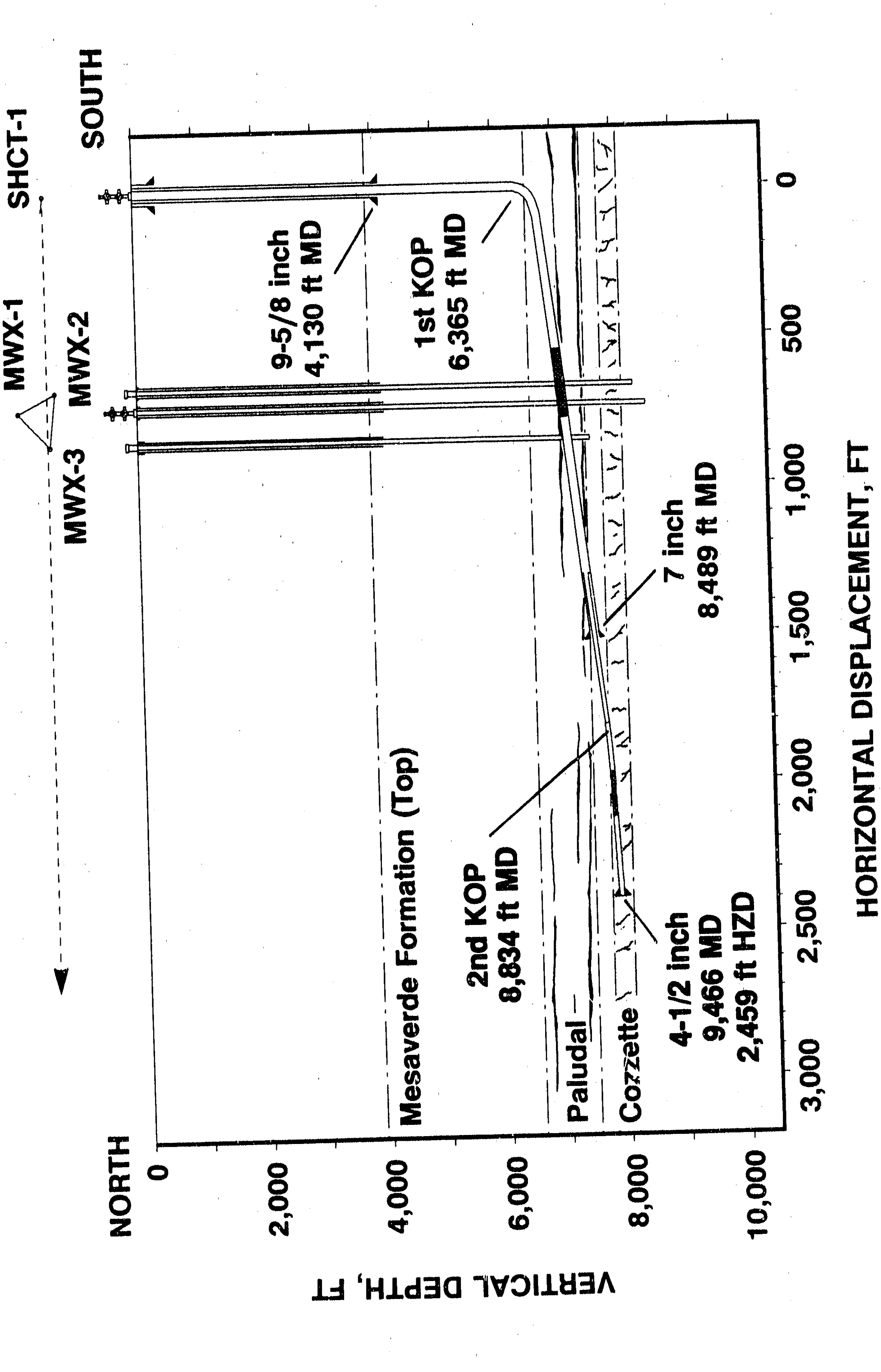

Figure 1. Slant Hole As Built Profile

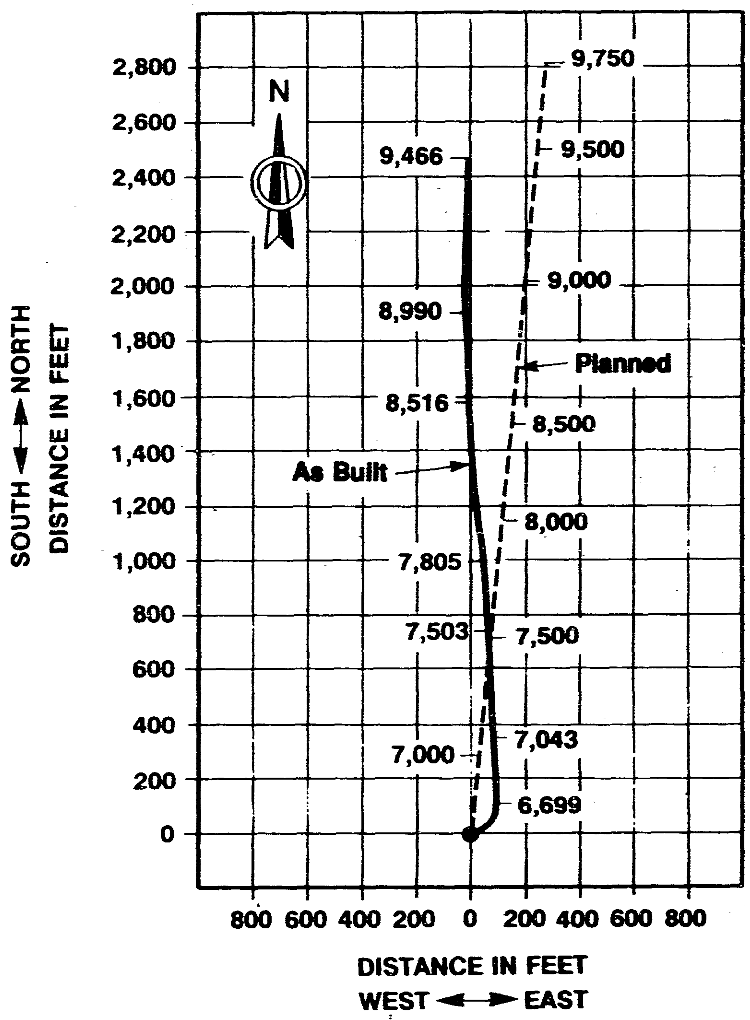

Figure 2. Plan View, Slant Hole Completion Test

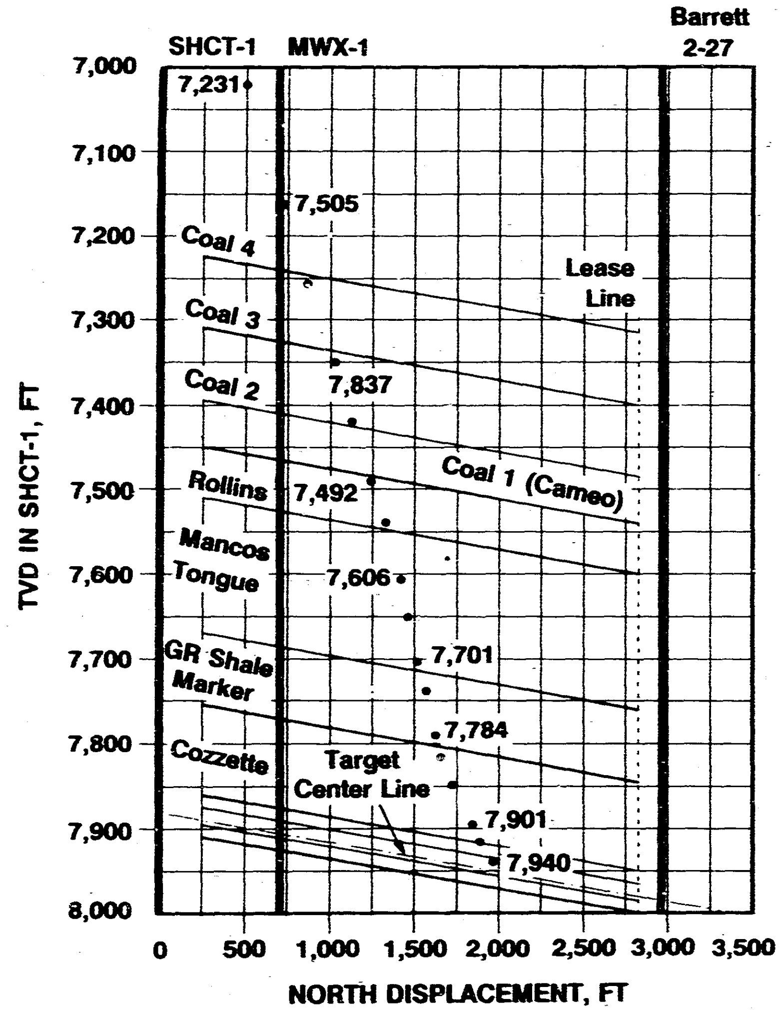

Figure 4. Wellbore Trajectory, Slant Hole Completion Test

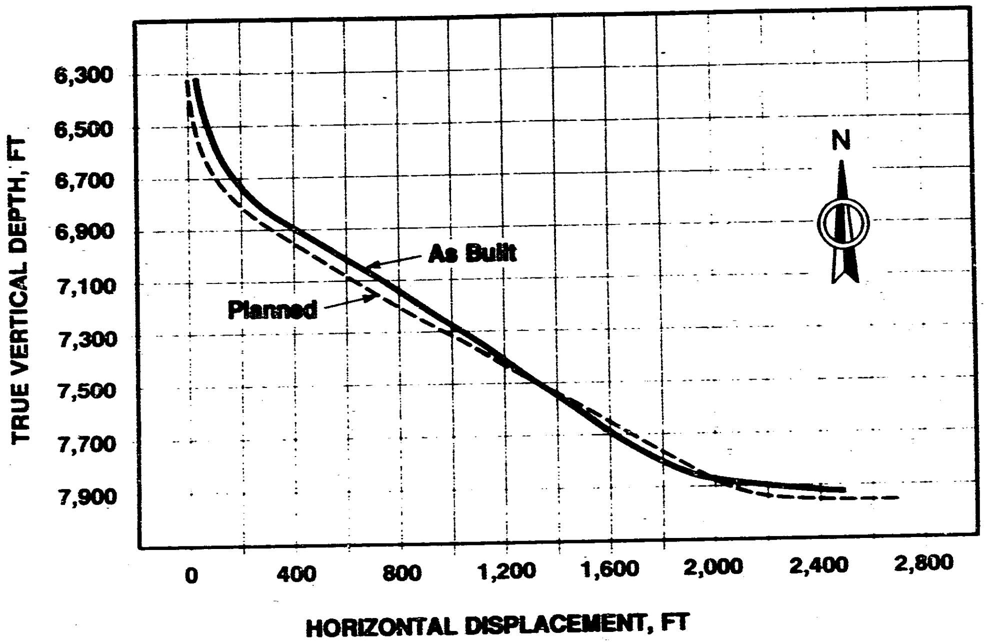

Figure 3. Profile View, Slant Hole Completion Test

Table 1. Coal Bed Gas Content Data

Interval	Depth, ft	Core Type	Gas Content, SCF/Ton
Mesaverde Coal	7,367 - 7,371	Conventional	543
Mesaverde Coal	7,371 - 7,380	Pressure *	765

*BHT = 170°F; BHP (7,090'TVD) = 4,900 psi

Table 2. Fracture Summary

		Mineralization			
Interval	Total Fractures	Quartz	Calcite	Quartz & Calcite	Non-Mineralized*
Paludal	45	2	19	1	23
Cozzette	35	24	1	10	0

*These may be fractures created by the stimulation of this zone in MWX-1.

Session 2

Unconventional Resources: Eastern Tight Gas

Eastern Tight Gas Project

Albert B. Yost II
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ABSTRACT

Research in the eastern tight gas project is a multidisciplinary effort that is directed toward developing a reserve base to help private industry provide a long-term supply of natural gas from Devonian shale, tight sands, coal seams, and other low-permeability formations located primarily in the Appalachian, Illinois, Michigan, Warrior, Richmond, Arkoma, and other basins located in the eastern, mid-continent, and greater southwestern areas of the U.S.

The low permeability gas-in-place contained in the eastern, mid-continent, and greater southwestern areas are 238, 8, and 188 trillion cubic feet (Tcf), respectively, according to a 1988 ICF-Lewin estimate.

The gas-prone, Devonian shales of the east underlie more than 174,000 squares miles of the Appalachian, Illinois, and Michigan Basins. Gas-in-place in the Appalachian Basin has been estimated by the U.S. Geological Survey to be 1100 Tcf, while the National Petroleum Council estimated 86 Tcf in the Illinois Basin and 74 Tcf in the Michigan Basin. DOE's estimate of technically recoverable gas for the Devonian shales in the Appalachian Basin is 61 Tcf if advanced case hydraulic fracturing technology is used.

The Federal Energy Regulatory Commission (FERC)-designated, tight sand resources in the Appalachian Basin are predominantly located in formations like the Big Injun, Berea, Benson, and Clinton Sands. Preliminary estimates of gas-in-place by DOE/METC for these formations totals 25 Tcf. Detailed assessment of the eastern tight sand resource is ongoing.

The coal seams of the eastern U.S. are located in the Northern Appalachian, Central Appalachian, Illinois, Warrior, and other small basins. These basins cover more than 139,000 square miles, and DOE has recently estimated that they may contain as much as 145 Tcf of gas-in-place.

The overall goal of the eastern tight gas project is to develop the scientific and engineering knowledge needed to increase the reserve base for eastern gas resources. More Specifically, the subprogram objectives are as follows: (1) identify and evaluate the resource/reserve base for eastern tight resources and develop a well-siting methodology to reduce dry hole risk; (2) conduct jointly funded, government-industry projects to test the applicability of gas recovery concepts to commercial production; (3) conduct cost-effective, geotechnical research in instrumentation, modeling, and tool development to reduce the cost of new technology; and (4) coordinate projects with GRI (Gas Research Institute) to ensure that respective research programs are complementary.

Resource-Characterization Research. Activities in resource-characterization research focused on developing cost-effective methodology for siting wells, using surface/subsurface geoscience mapping techniques to increase production from fractured reservoirs and to reduce dry hole risk. As the scope of the eastern gas subprogram expands from specifically Devonian Shale to other low permeability formations, a renewed effort in identification of resource/reserves will be initiated. Tight gas will be assessed for the Appalachian Basin, all eastern gas subprogram basins will be identified, and publically documented resource/reserves will be identified.

A new thrust will be initiated in FY91 for fracture reservoir mapping aimed at development of a cost-effective method to identify high-grade fractured reservoirs in the absence of drilling a new well.

Production Technology Research. Ongoing efforts in production technology research focus on drilling, logging, stimulation, and testing the Columbia Natural Resources, Inc. (CNR) horizontal well in Calhoun county, West Virginia during FY91 and the stimulation activities associated with the CNR horizontal well in Martin county, Kentucky. In addition, introduction of a new fracturing process using carbon dioxide and sand will continue in up to 15 Devonian Shale wells in various areas of the Appalachian Basin. The stimulations will be performed in wells of opportunity that Industry is currently drilling in the Basin. Three, multi-strata, completion project wells will be drilled during FY91 in Raleigh county to verify the production analog and to assess the economics of multi-strata completion technology. A new request for proposals (RFP) for horizontal wells in other, low-permeability gas reservoirs is being evaluated prior to award of up to 5 cost-sharing contracts with Industry. The purpose of these contracts is to evaluate the merits of improving gas recovery efficiency through multiple hydraulic fracturing of long, horizontal wells in low-permeability formations.

Geotechnical Supporting Research. Ongoing efforts in geotechnical supporting research include in-house, systems engineering studies in gas storage, risk analysis and economics of horizontal drilling, reservoir and stimulation analysis of carbon dioxide/sand frac field tests, and data base activities associated with resource/reserve studies of low-permeability gas formations. In addition, ongoing efforts aimed at improving the current hydraulic fracturing codes will continue.

Accomplishments in FY 90 includes the following activities and results:

> Completed site selection, drilling, logging, and stimulation of a 2000-foot long, horizontal well in Putnam county, West Virginia. Results of the project include reducing drilling cost from 5 to 2.5 times the cost for a vertical well; reduced drilling time from 58 days to 31 days at a saving of $270 thousand per well; identified measurement while drilling (MWD) as an unresolved problem in improving drilling efficiency; experienced no motor failures during the entire operation; verified that the siting methodology used by the METC geoscience group reduces dry hole risk; and identified limitations of selected, completion equipment available for horizontal wells.

- Completed site selection, drilling, and logging of a 2000-foot long, horizontal well in Martin county, Kentucky. Results of the project indicate high natural production (1400 thousand cubic feet [Mcf]/day) compared to vertical wells in the area but prior to stimulation; successful run of new completion hardware to permit zonal isolation; gained credibility for METC geoscience mapping methodology; tested and verified operating life of a new, industry prototype, MWD system for air drilling; and show-cased project for completion technology and running motors using air drilling.

- Completed site-selection activities in support of drilling a third horizontal well in Calhoun county, West Virginia with Consolidated Gas.

- Initiated the testing and introduction of a new hydraulic method using carbon dioxide and sand. A multi-year, 24-well program has been initiated to introduce this new fracturing process to the Devonian Shale. This new process is a non-damaging, fracturing process that eliminates the harmful effects of using a water-base, fracturing fluid.

- Completed the development of a production analog and site-selection activities associated with the Multi-Strata Completion Study. Gas resources in Raleigh county, West Virginia have been identified and evaluated for geologic and petrophysical parameters that control production. Coal gas content, coal isopach, structure-trend surface, permeability, and combined resource maps were used to develop the production analogs for this project.

Hydraulic Fracturing of the Devonian Shale With a Non-Damaging Fluid

CONTRACT INFORMATION

Contract Number	DE-AC21-90MC26025
Contractor	Petroleum Consulting Services P. O. Box 35833 Canton, Ohio 44735 (216) 499-3823
Contractor Project Manager	Raymond L. Mazza
Principal Investigators	Raymond L. Mazza James B. Gehr
METC Project Manager	Albert B. Yost II
Period of Performance	May 5, 1990 to February 5, 1992

Schedule and Milestones

FY91 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
1.1 Work Plans	---	---	---	---	---	---	---	---	---	---	---	---	---
1.2 Pre-Frac		---	---	---	---	---	---	---	---	---	---	---	---
1.3 Fracturing				---	---	---	---	---	---	---	---	---	---
1.4 Post-Frac					---	---	---	---	---	---	---	---	---
1.5 Prod Mon					---	---	---	---	---	---	---	---	---

OBJECTIVES

Overall: The Phase I base program investigates the effectiveness of hydraulically stimulating an Appalachian Basin, tight, fractured, Devonian Shale interval with a non-damaging fluid - carbon dioxide (CO_2) and sand by comparison of the resulting gas production with that from nearby conventionally stimulated wells. It includes up to fifteen (15) wells in up to five (5) target areas located in Kentucky, Ohio, Tennessee, Virginia, and West Virginia.

Task 1.1 Target Area Work Plans

To identify five (5) individual target areas where up to a three (3) well stimulation test can be performed and the gas production compared with that existing conventionally treated nearby wells.

Task 1.2 Pre-Frac Field Activities

Conduct pre-frac activities such as natural production measurement and the associated flow entry point identification, cement bond logging, perforation placement, etc.

Task 1.3 Fracturing the Candidate Wells

Design and implement the fracturing treatment on the candidate wells in conjunction with operators, service companies, and DOE design criteria.

Task 1.4 Post Frac Field Activities

Well cleanup and/or post frac gas production monitoring.

Task 1.5 Production History Monitoring

Monitor and compare the production history from the candidate well with that from existing nearby wells.

BACKGROUND INFORMATION

The hydraulic fracturing of underground strata to produce natural gas and oil is generally performed either with liquids (generally water or water based foam) which convey sand proppant, or with gaseous nitrogen without proppant. Both procedures have some undesirable aspects when the Devonian Shale is treated.

The Devonian Shale in many areas is sensitive to water - which can impede gas flow. Sometimes the Devonian Shale is stimulated with nitrogen to eliminate the blockages resulting from the presence of water. This procedure is non-damaging because nitrogen is inert but is undesirable because proppant cannot be transported, and in some areas the fracture can close, negating the process by restricting or stopping the gas flow.

This procedure provides a hydraulically created fracture through the application of a non- damaging liquid which also transports proppant thereby preventing the fracture from closing. The fluid is carbon dioxide (CO2) which is maintained in a liquid phase by elevating the pressure during the treatment and later allowing it to vaporize as the formation warms it and the pressure is reduced.

The liquid CO2 and sand stimulation treatment requires a specially designed blender which contains the sand in a closed vessel where it is slurried with liquid CO2 at a pressure of 250 to 300 psi. The blender has a capacity of up to 70,000 pounds of sand, although this proposal is utilizing a blender with a <u>reduced</u> sand capacity of 48,810 pounds.

Canadian Fracmaster, a Canadian based oil field service company (Calgary, Alberta, Canada), has designed and patented a blender to perform these services. They routinely perform this type of stimulation treatment as well as others, and have executed more than 1100 of these CO2/sand treatments. Presently there is no oil field service company in the U.S. that can efficiently blend and pump sand with liquid CO2 because their blenders are open to the atmosphere and the sand cannot be mixed with the liquid CO2 under pressure. The increased pressure of the Fracmaster closed system blender is necessary to increase the fluid viscosity, thus enabling it to transport sand. There have been some attempts to use existing equipment, and there have been some relatively small quantities of sand mixed and pumped without water, but these treatments have been limited in size and unable to prop any fracture of significance.

PROJECT DESCRIPTION

This project involves the

demonstration of this technology in the U.S. by arranging for Canadian Fracmaster's closed system process to blend liquid CO2 and sand to hydraulically stimulate the Devonian Shale. The expense of bringing all of the associated equipment (bulk and pump trucks, etc) is prohibitive. Consequently only the blender is being sent and it will be used in conjunction with conventional, U.S. based pumping equipment.

Canadian Fracmaster will assist in the engineering design, technical expertise, and provide on-site field supervision of the field operations.

The post treatment production history will be compared with the background production data gathered previously from nearby wells and differences in clean-up and production rate will be evaluated.

Selection Criteria

The selection criteria are that:

1. The candidate well is situated in an area of established gas production from the Devonian Shale.
2. The well must produce exclusively from the Devonian Shale.
3. Sufficient historical gas production data from nearby wells is available to evaluate the response to the CO2 stimulation process.
4. The well be placed in production shortly after the stimulation to enable the evaluation to begin.
5. The well be allowed to produce in an uninterrupted condition, i.e, in the absence of seasonal pipeline shut-ins, etc.

Selection Process

The selection process includes identifying and contacting those operators with ongoing drilling programs within the areas of established Devonian Shale production. It then involves meeting with the operators to (1) describe the program, (2) determine if the operator is interested in participating, and (3) determine if viable candidate wells will be offered. At that time it is also determined that the timing is suitable to both the operator and the Department of Energy (DOE) (Figure 1).

Once the selection process progresses to this point the offset well treatment and production information is combined and summarized in a standardized format (Figures 2, 3). The information includes the casing and completion programs, reservoir pressure, and open flow information along with a production history plot (Figure 4) which are submitted to the DOE for approval. They are then either accepted, rejected, or additional information is requested. Once the DOE approvals are obtained the treatments are sequenced with the operator's schedule.

RESULTS

The project work commenced on May 5, 1990 and the efforts to date have been directed towards identifying candidate wells in areas of established Devonian Shale gas production with willing operators with current drilling plans (Task 1.1), and to a lesser extent developing work plans and designing treatments (Task 1.2).

Additionally, this stimulation process has been discussed with Canadian Fracmaster in detail. Also, a number of Canadian operators familiar with these treatments were interviewed to address the suitability of the process to the Appalachian Basin Devonian Shales.

1. The blender has been prepared for shipment to the eastern U.S.

* Escrow agreement in place
* Replaced all valves
* Rebuilt power unit
* Partition installation - to reduce CO_2 requirements
* Painting
* Field testing - Four (4) jobs have been run and the blender is ready for delivery

2. Met with Canadian operators that have used this process to evaluate its effectiveness and appropriateness with procedural recommendations for Devonian Shale treatments.

3. Met with U.S. based service companies regarding interfacing with Canadian Fracmaster's blender and providing pumping services.

4. Negotiating the cost of CO_2 independently.

5. Identifying target areas and upcoming drilling activity. Eastern Kentucky and southern West Virginia are considered prime target areas.

   * Twelve (12) operators have been contacted.

   * Five (5) may have plans to drill Devonian Shale wells of interest.

   * Five (5) have plans to drill Devonian Shale wells of interest.

   * Five (5) (of the five (5) with drilling plans) are interested in participating.

   * Four (4) have supplied information.

   * Three (3) well packages (5 wells) have been prepared and submitted to DOE for review.

     Kentucky - 1 operator - 2 wells (1 withdrawn because of schedule).

     West Va - 2 operators - 3 wells

   * Three (3) packages have been reviewed and discussed with DOE

   * A more detailed review of the packages has been requested and is underway.

   All of the operators are anxious to proceed as soon as possible. Some have been in contact with Canadian Fracmaster regarding job design.

6. Have reviewed oil and gas regulations in all five (5) states and an Environmental Assessment is being prepared and revised per DOE request.

Comment:

This could be a pivotal year in Devonian Shale drilling activity because of uncertainty regarding the extension of the Sec 29 tax cedit which is essential to Devonian Shale well economics. Consequently, many operators are drilling before year end. The drilling activity and therefore the number of wells of opportunity available for this program could be greatly reduced after December, 1990 if the credit is not extended.

FUTURE WORK

* Continue solicitation of wells of opportunity

* Proceed with fracturing before year end and commence production evaluations.

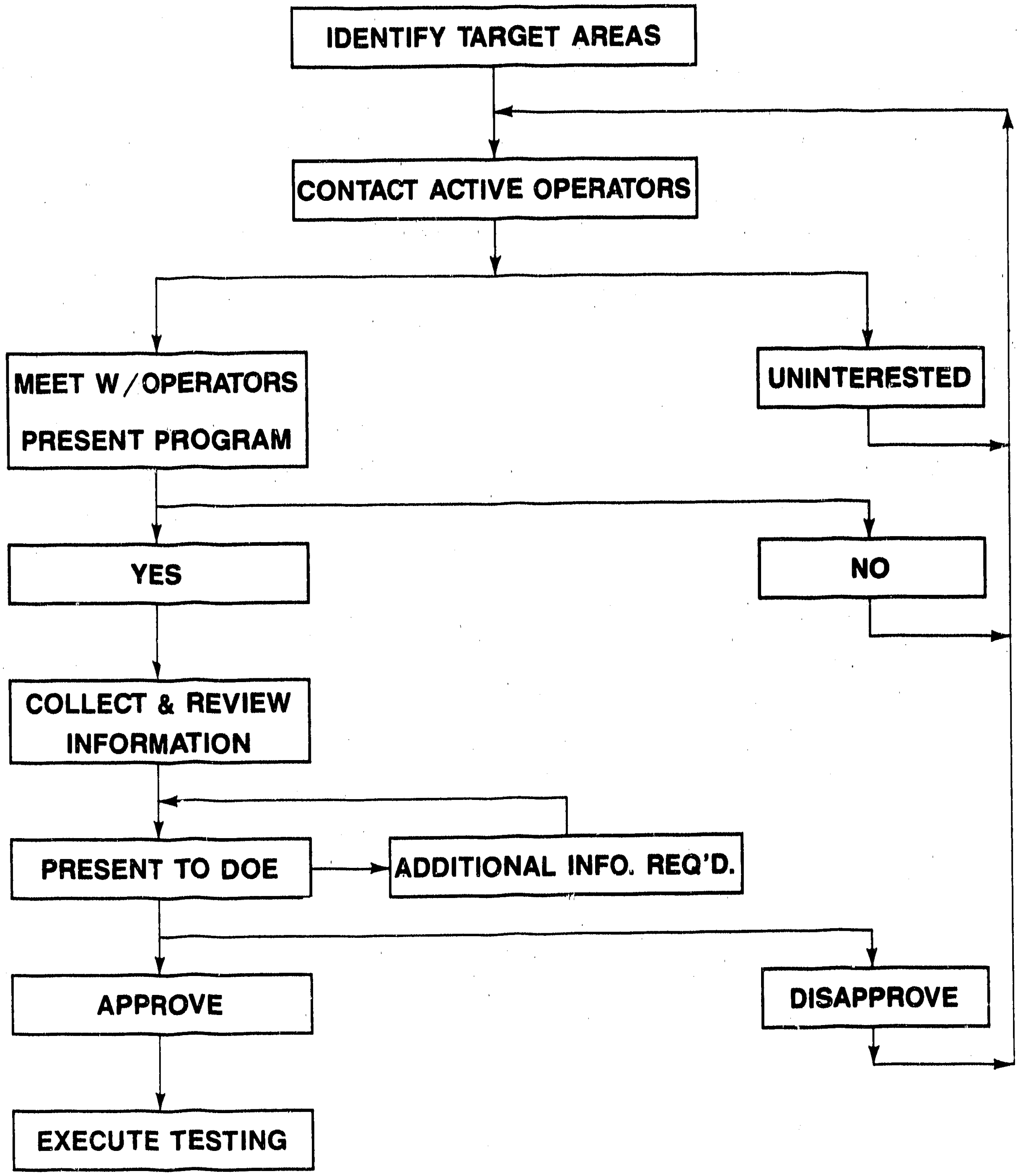

Figure 1. Selection Process

Production Summary

WELL:	AA ARBUCKLE #615	OPERATOR: HALLWOOD (QUINOCO)
TARGET:	SHALE	CONTRCTR:
WATERSHED:	18MI CK	RIG #:
QUAD:	WINFIELD SE	PERMIT #: 47-079-0607
DISTRICT:	UNION	ELEV GL: 812.70
COUNTY / ST:	PUTNAM / WV	ELEV KB:

DATE	GAS PROD	
	MCF	CUM
Dec-56	4218	4218
Dec-59	14247	31916
Dec-62	12908	72648
Dec-65	10852	108288
Dec-68	14123	145751
Dec-71	10966	183384
Dec-74	13343	219848
Dec-77	11300	256812
Dec-80	5852	282540
Dec-83	6825	301556
Dec-86	3827	317534
Dec-89	6711	333341

Figure 2. Production History Summary

Production Summary
47-079-0607

AA Arbuckle #615

				h	SUB SEA	
DRILLED:	06/15/56 - 08/31/56					
TOTAL DEPTH:	4175					
FORMATION:	SALT SAND	1735	1825	90	922	1012
	BROWN SHL	3722	3775	53	2909	2962
	GAS	3725	1/10W-1"			
	BROWN SHL	3920	4025	105	3107	3212
	GAS	3930	2/10W-1"			
	GAS	4025	2/10W-1"			
	BROWN SHL	4060	4160	100	3247	3347

WATER-FRESH 115 WATER-SALT 1030 (0.5BPH)
1670 FULL HOLE

CASING-CONDUCTOR: 16.000IN @ 24 FT w/ ?SXS
CASING SURFACE:
CASING-PRODUCTION: 7.000IN @ 2547FT w/15SXS
LINER: 5.500IN X 531FT

COMPLETION: SHOT 3708-4175FT w/5000 lbs GELATIN - 08/31/56

PRESSURE: 880PSI (72HRS)
OPEN FLOW: 198MCFD (N/R HRS) BEFORE SHOT = 23.6MCFD

Figure 3. Production Summary

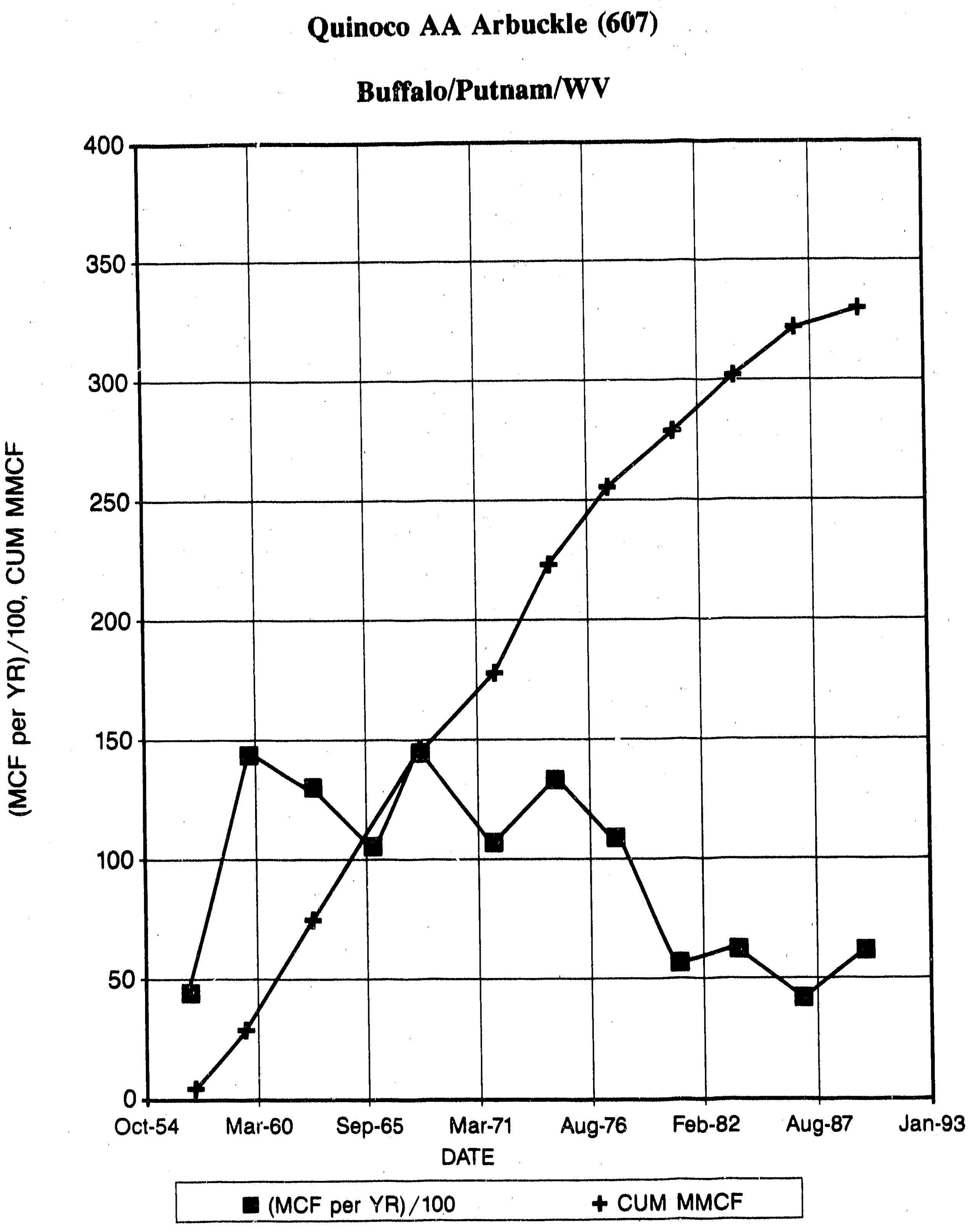

Figure 4. Production History Plot

Multi-Strata Exploration & Production Study

CONTRACT INFORMATION

Contractor Number DE-AC21-89MC26026

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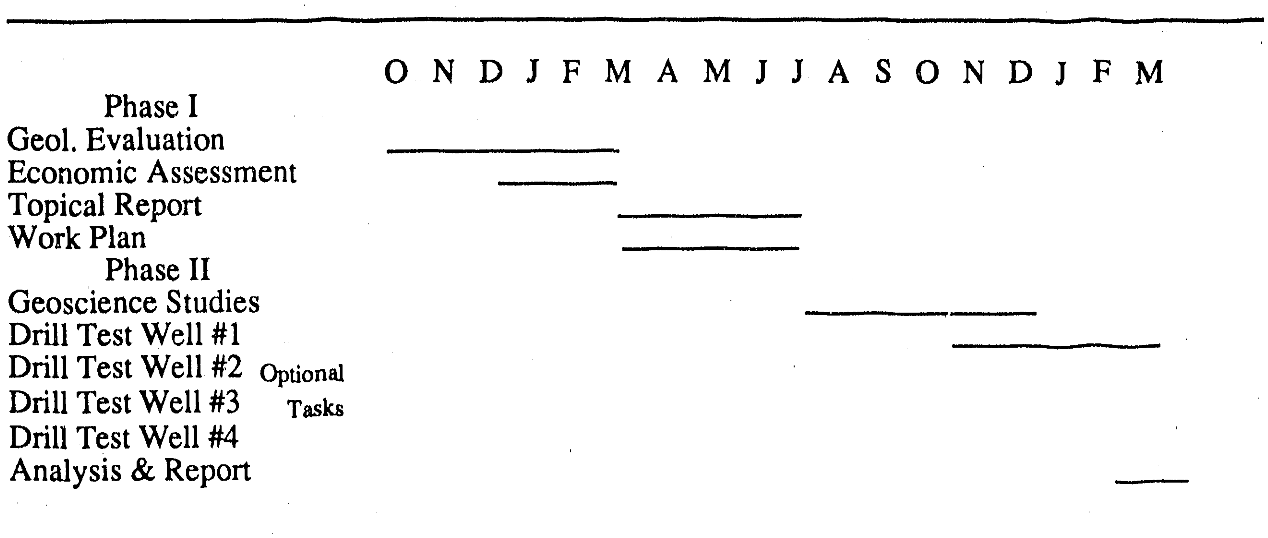
Period of Performance October 15, 1989 to March 21, 1991

Schedule and Milestones

FY 89-90 Program Schedule



OBJECTIVES

The objectives of this project are to: demonstrate low-cost exploration techniques in a relatively lightly developed area of southern West Virginia;

- add significant by-passed methane reserves to the traditional natural gas base recognized in the conventional Mississippian and Pennsylvanian reservoirs;

- demonstrate state-of-the-art engineering designs for well completions that would allow production of both the natural gas and methane from a single wellbore simultaneously;

- analyze, evaluate and demonstrate to industry the economics of such a program on a full scale basis in an area with both coal and conventional shallow natural gas reservoirs.

BACKGROUND INFORMATION

Beckley College, a community college in Beckley, West Virginia, supported by BDM Engineering Services Company (BDM), with offices in Morgantown, West Virginia, has received a contract from the Department of Energy (DOE) for a research program that will develop a new approach for siting exploration wells, using a geostatistical methodology, analyzing publicly available data bases quickly and cost-effectively, and that will design production methodologies that can be used to recover both conventional natural gas from traditional reservoirs and coalbed methane from shallow coal seams, using a single wellbore.

PROJECT DESCRIPTION

The area selected for the project was Raleigh County, West Virginia, a region with extensive coal reserves in multiple seams at varying depths, including coals at depths that are unlikely to be mined in the foreseeable future. Natural gas production is known from several shallow Mississippian and Pennsylvanian units in the study area ranging in depth from a few hundred feet to almost 5000 feet.

The project has been divided into two phases, the first concentrating on research into the geology of the area and reserve and economic assessments of the resource in place, and on engineering design. The second phase will involve site-specific detailed geoscience testing and the actual application of the design work with a drilling program.

The geologic studies and the preliminary engineering work for Phase One have been largely completed, at this time, and the location of the initial test site is being finalized, a task which involves answering legal questions of ownership and lease status.

The Geostatistical Exploration Methodolgy

Work on this project began with the collection of an extensive, non-confidential data base assembled from inexpensive, publicly available sources. The information obtained included geologic, engineering, ownership and production data on a large number of wells in the study area.

Charts, tables, graphs and over one hundred geologic, engineering, production and reserve maps were made, based on this information. A CADD program was used to prepare local map bases which were double-checked in detail for the accuracy of well locations. Key revisions were made to the bases to ensure accuracy. Initial mapping was done using computer mapping programs. The resultant maps were hand-revised and additional, manually-contoured maps were prepared. The results presented a comprehensive picture of the geology and reserve picture of the units from the coal measures down through the Mississippian Big Lime formation.

Below the top of the Greenbrier "Big Lime" formation, the amount of data available quickly diminished, but sufficient control was still present to prepare several regional structure and isopach maps from which a reasonably detailed pre-Big Lime geologic history of the area could be reconstructed.

Using the data base and maps, the geology of the area was interpreted, concentrating on the potential reservoir formations. Initial environments of deposition were determined for each target formation, and the available information on the lithologies of the key units in the region were studied to identify the diagenetic modifications that had enhanced, degraded or destroyed the reservoir quality in various portions of the maps.

Additionally, remote-sensing and geoscience studies were planned for key areas, to confirm the tectonic history of the region. These studies could not be conducted until access was gained to the proposed well sites. Work is beginning on this phase of the project at the present time.

Using all of these sources of information, a tripartite geostatistical study was conducted with gas resource (including coalbed methane, as well as conventional natural gas), the reservoir (including development, quality and history), and structure (including tectonic fracturing) as the three poles. The results from this work were cross-checked with a second test approach, using the depositional environment as one pole, diagenetic modification as the second, and tectonics as the third. Triangle diagrams were prepared outlining the methodology.

The resource base included the elements of coalbed methane, Pennsylvanian natural gas sources and Mississippian natural gas sources. The reservoir component was divided into original, enhanced and degraded elements. Structure was subdivided into active, passive and fractured features.

The various data were plotted on the well bases and geostatistically optimized plots were prepared showing the best areas where one could expect to encounter:

- coalbed methane, prior to and after mining;
- natural gas for each potential target formation;
- enhanced reservoir quality;
- degraded reservoir quality;
- intensely fractured areas.

Composite maps were prepared incorporating all of these geologic elements. This allowed the identification, geostatistically, of areas that mathematically optimized the chances of encountering both commercial quantities of coalbed methane and natural gas reserves in the shallow conventional reservoirs.

Results

The studies of the coal showed that numerous thick and thin seams were present under the study area quadrangles. All but two of these, the Pocahontas #3 and the Beckley Coals, were eliminated from consideration as realistic drilling targets under the guidelines being applied in this program. Both total coal seam thickness and depth of burial had to meet or surpass key threshold levels to be included in the list of potential drilling targets, so several shallow seams were ignored as primary targets for this program. A watch will be kept during drilling of the test holes to look for other possible deep, thick coals that could contribute commercial amounts of methane.

Structure and mine maps of the coal showed several areas where faulting and/or fracturing appeared to be present, affecting the shallow section and producing severe disturbances within the coal. Such fractured areas should readily yield the entrapped methane, with numerous migration routes along the extensive fracture networks. In addition, an area was identified which appears to have been a high block during the time of Beckley Coal deposition. This proved to be a very interesting area which became the focus of later studies.

Among the conventional Pennsylvanian and Mississippian reservoirs, two units, the Ravencliff Sandstone and the Greenbrier "Big Lime" Limestone, were identified as key target intervals. Several other units have had limited production histories over rather restricted areas, but the Ravencliff and "Big Lime" units were the only two producing formations with wide extent that merited serious study within the guidelines of this project. Other formations will be monitored during drilling to watch for other potential production in the test hole.

The Ravencliff unit is a fluvial sand that was laid down in a series of long, sinuous channels that cross Raleigh County. These channel sands were massive, clean deposits originally, exceeding 180 feet in thickness in places. The channels meandered back and forth across the study area, leaving behind excellent reservoirs in point bar deposits. The channels cut deeply into the floodplain and deeper portions of the channels have frequently been misscorrelated in logs as "Maxon" Sands.

The original porosity in the Ravencliff was so good that it became its own worst enemy. The cleanest portions of the Ravencliff were penetrated by mineralizing fluids at an early date with extensive clay deposition and pore filling and clogging. Much of the original Ravencliff porosity in the central channel areas has been destroyed. The study of the Ravencliff focussed on identifying backchannel and other isolated areas with remnant porosity.

The other major reservoir, the "Big Lime", contains good gas reserves in areas where the "Big Lime" seafloor had shoaled and where wavebase rolled the mud up into pelletized balls in oolitic zones.

Interestingly, the high block identified by the thin and "no coal" area in the Beckkey Coal seam seems to coincide with the area of shoaling during "Big Lime" time. This implies the possibility of reactivation of a deep-seated feature in this area. The regional isopach work, as well as Oriskany and Tuscarora drilling patterns show that the block had been high over a very long period and was probably reactivated a number of times during the Paleozoic era.

Fracture studies helped in outlining the margin of this block. An extensive network of coal disturbances and pinchouts, fracture trends, lineament segments and better natural gas wells all seemed to occur along this trend. The final proposed test well locations all fell along or near the margin of this block where there was still some Beckley Coal left and where there were indications of oolitic "Big Lime" limestone beds.

Reservoir Engineering

Extensive reservoir analysis and modeling were performed on the data base wells to determine the nature and quality of the various producing units. Reserve studies and decline curve analyses confirmed the potential for the conventional resource in the selected target area.

Reservoir quality maps were produced showing the reserves to be expected in various areas, the reserves that should be producible over various periods of time, the time to economic payout and anticipated economic life of the various wells, and the total resource in place for conventional natural gas over the study area.

Engineering Design

Preliminary work has been done on the engineering design for the initial test hole, although the numbers cannot be finalized until the precise location and elevation of the well are confirmed.

No significant problems are anticipated in this design, although it will include the equipment and production strings necessary to isolate the production of methane from the conventional gas resource. It is expected that this isolation will be necessary for research purposes and to properly allocate payments to the coal owners and to the oil and gas lease holders.

It is anticipated that it will be possible to directly commingle the methane and natural gas for marketing purposes.

Current Project Status

At present, the scientific and engineering investigations are nearly complete, and several preliminary proposed well locations have been selected. These sites were chosen solely for their reservoir quality, without regard to mineral ownership considerations. Negotiations are now proceeding with the various resource owners and/or leaseholders for the rights to drill and co-produce the methane and conventional natural gas at the selected locations. No major problems are anticipated with these negotiations at this time.

It is hoped that drilling will begin in a matter of weeks on the first test hole.

Measurement-While-Drilling (MWD) Development for Air Drilling

CONTRACT INFORMATION

Contract Number:	DE-AC21-88MC25105
Contractor:	Geoscience Electronics Corporation 725-A Lakefield Road Westlake Village, CA 91361
Contractor Project Manager:	William H. Harrison
Principal Investigators:	William H. Harrison Llewellyn A. Rubin
METC Project Manager:	Albert B. Yost II
Period of Performance:	September 30, 1988 to January 30, 1991

SCHEDULES AND MILESTONES

PHASE II/III Program Schedule (FY 1990)

	O	N	D	J	F	M	A	M	J	J	A	S
Field MTBF/Tool Reliability Verification Tests:												
Field Test No. 3	—	—										
Field Test No. 4			—									
System Modifications				—	—	—	—	—	—			
Search For Wellbores of Opportunity										—	—	—

PHASE III Program Schedule (FY 1991)

	O	N	D	J	F	M	A	M	J	J	A	S
Field MTBF/Tool Reliability												
Verification Tests:												
Field Test No. 5	—	—										
Final Report Draft		—	—									
Final Report Final				—								

OBJECTIVES

This program is being conducted under cost-sharing contract No. DE-AC21-88MC25105 with the U.S. Department of Energy, Morgantown Energy Technology Center (METC).

The program is entitled "Measurement-While-Drilling (MWD) Development for Air Drilling," and is being performed by Geosciences Electronics Corp (GEC).

The objective of this program is to tool-harden and make commercially available an existing wireless MWD tool to reliably operate in an air, air-mist, or air-foam environment during Appalachian Basin oil and gas directional drilling operations in conjunction with downhole motors and/or (other) bottom-hole assemblies. The application of this technology is required for drilling high angle (holes) and horizontal well drilling in low-pressure, water sensitive, tight gas formations that require air, air-mist, and foam drilling fluids.

The basic approach to accomplishing this objective is to modify GEC's existing "Cableless"™ MWD tool to improve its reliability in air drilling by increasing its tolerance to higher vibration and shock levels (hardening). Another important aim of the program is to provide for continuing availability of the resultant tool for use on DOE-sponsored air-drilling programs.

The Contract requires the effort to be accomplished in three phases. Phase I took 14 months to complete. The hardened MWD tool was required to meet the following minimum requirements:

- System MTBF, 50-hours.
- Maximum depth (TVD) of 10,000 feet.
- Battery life in excess of the tool MTBF.
- Operational in rotary drilling and downhole motor scenarios.
- Operate in hole diameters from 6-1/4 to 10-5/8 inch.
- Data transmission rate of 1 bit/second, minimum.
- Operating temperature 135°C, maximum.
- Directional data provided on azimuth, inclination, and tool face.
- Operate in typical air flow rates of 1,500 to 3,000 CFM, and mist or foam rates from 10 to 30 barrels per hour.

Phase I was aimed at evolving GEC's existing Model 20-C MWD System into a hardened-for-air-drilling MWD tool. The program includes extensive field testing to verify that the target 50 hour (MTBF) has been achieved. This evolved hardened tool has been designated the Model 27 MWD.

Specifically, in Phase I, GEC embarked on a program to

- Complete the design of the Model 27 with respect to reliability, shock, vibration, user requirements, and sizes of drillpipe.
- Upgrade two Model 20C MWD systems to Model 27 field operational prototypes.
- Field test the Model 27 tools in air-drilling controlled environments. Evaluate performance and any failures.

Phases II and III were optional, and provided for additional field test opportunities.

BACKGROUND STATEMENT

In the last few years, the need for reliable, low cost, directional drilling services in air drilling scenarios has become widely recognized. Attempts at using directional drilling systems that were designed to operate in mud have resulted in less than satisfactory performance when operated in air. The severe shock and vibration environment of air operation compared to mud operation immediately extracted a toll in reduced reliability. Mud pulse MWD tools, in general, perform marginally when operated on air and may not be viable. Even though some wireline steering tools have been made to operate reliably in air, the logistics and cost of operating with a wireline are frequently unacceptable.

In 1985, a Model 27 predecessor, the Model 20B "Cableless Steering Tool" successfully underwent extensive field-testing and operational evaluation, primarily high-angle drilling at THUMS, Long Beach. Later, during the Summer and Fall of 1986, the Model 20-B was utilized by DOE Contractor, BDM, on two occasions to evaluate its applicability to air-drilling in the Devonian Shales. This project provided GEC its first experience of the rigors of air drilling. A combination of mechanical failures and computer software problems forced an early withdrawal of the tools. The primary cause of the mechanical failure was thought to have been the lack of viscous damping and lateral support of the downhole sensor/electronics unit. In ordinary mud drilling, the fairly viscous mud itself provides a modicum of damping to the high-"Q" distributed spring-mass system that is the drill-string and its contents. While the excitation is primarily in the longitudinal axis (and probably no higher than in mud drilling), the damage appears to result from higher-levels of shock and vibration in the transverse axes. The mud appears to provide greater damping in the transverse axes than in the longitudinal axis.

At the conclusion of the tests, GEC undertook a program to improve the tool design by evolving it to the next generation, Model 20-C "Cableless Steering Tool". The Model 20C had significant improvements in the electronics and power units which contributed to improved reliability and operability. Nonetheless, it was recognized that additional hardening and testing was needed to achieve the reliability to meet DOE's air-drilling requirements.

PROJECT DESCRIPTION, PHASES II & III

Phases II and III were Contract Options for additional field testing which were exercised during FY 1990 and FY 1991. Phase II provided for certain minor modifications to the system, and two field tests in Devonian Shales. During these two field tests, it was determined that the system performed poorly in wellbores in very dry formations that were drilled with dry air.

In the transition from Phase II to Phase III, recommendations for improvements were made and some approved. These were implemented in the time-frame March-June, 1990. The remaining program tasks are Field Test No. 5, and the Final Report. All work must be complete by end of January, 1991. A suitable wellbore of opportunity for Field Test No. 5 has been in progress since July, 1990. Only recently was a suitable site located and committed to. The window of opportunity was to be early November, but a speeded-up drilling schedule had the last well in the series spudded in late October.

RESULTS

The first two field tests, conducted over coal mines near Oakwood, Virginia during May and July, 1989, produced over 197 hours of in-hole operation on the Model 27's, with 116 hours being actual drilling. During this time, 4 primary failures occurred, which precipitated 4 secondary failures. The resultant MTBF's were 49.2 hours in-hole, and 29 hours while drilling. The while-drilling MTBF from Test 1 was 19.63 hours, and from Test 2, 38.61 hours, against a Contract goal of 50 hours.

The last two field tests, (FT 3, 4) produced over 80 hours of in-hole operation on the Model 27's, with 44 hours comprised of actual drilling. During this time, 2 primary failures occurred. The while-drilling MTBF from Test 3 was 21.88 hours. These tests were conducted in West Virginia in Devonian Shales areas in the time frame October through December 1989.

The most important result of these two field tests was the discovery of system signal-margin inadequacies associated with dry-air-drilling of very-dry formations. No electric logs were evaluated before these holes were drilled. Further, because of extensive equipment failure on FT #3, only sketchy results were obtained. It appeared that the configuration of the Model 27 MWD System in use, was unable to provide the desired results in wellbores having extremely dry conditions at the BHA. In addition, after obtaining and examining electric logs from these holes (or nearby holes), it was noted that in a major interval between the surface and the desired pay zone ("Big Lime"), as well as in the pay zone, the formations exhibit very-high resistivities (several hundred ohm-meters compared with an average of 30-50).

The problems enumerated above were excerbrated by use of insulating oil for lubricating the downhole motor in FT 4. This may have given rise to even poorer electrical contact between the lower portion of the BHA and the surrounding rock, resulting in total loss of received-signal below about 4000 feet. Following FT #4, it was determined that several steps needed to be taken to compensate for the dry rock and oil problem downhole. After discussions with oilfield personnel, the following steps, constituting Phase III of the Contract, were taken:

- The Model 27 power amplifier was modified to match higher impedances that have been regularly encountered in the tests,
- Substitutes for the downhole motor lubricant, that are electrically conductive (including graphited motor oil) were determined and obtained, and
- A tradeoff study of employing a longer electrode (e.g. 60 feet vs 6 feet) for the signal-current return was performed.

In addition, steps were taken to improve the mechanical reliability of the joiner-tube interconnecting cables, by changing the "put-together" scheme from circumferential threads to non-rotating-joint circumferential lock pins.

FUTURE PLANS

Filed Test No. 5: A field test in dry formations is planned, in which several comparative situations can be evaluated by adding small amounts of water, or conductive oil into the drilling process. The operational problems and effectivity of the longer electrode will also be evaluated. This is planned for November, 1990, assuming a suitable wellbore can be obtained.

Final Report: This task covers preparation of the Final Report in conformance with the Contractual requirements, and a Tool-User's Manual for use in training new operators.

REFERENCES

Rubin, L.A., and Harrison, W.H., "Downhole Telemetry Apparatus and Method," US Letters Patent No. 4,691,203, issued 9/1/87.

Harrison, W., "Measurement-While-Drilling (MWD) Development for Air-Drilling, Proceedings of the Natural Gas R&D Contractors Review Meeting, U.S. Department of Energy, DOE/METC-89/6103 (DE89011683), 4/18-19/89.

Rubin, L. and Harrison, W., "Wireless Electromagnetic Borehole Communications, A State-Of-The-Art Review," Proceedings, Measurement While Drilling Symposium, Louisiana State University, 2/26-27/90.

Harrison, W., Mazza, R., Rubin, L. and Yost, A., "Air-Drilling, Electromagnetic, MWD System Development," Proceedings of the 1990 IADC/SPE Drilling Conference, 2/27/90-3/2/90, (SPE #19970).

Results of Horizontal Well Site Evaluations in Fractured Devonian Shale Reservoirs

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SUMMARY

Several geologic mapping techniques, including geophysical and geochemical surveys, are used to define the orientation and production potential of fractured fairways in the Devonian shales. A flow sheet (Figure 1) was developed to evaluate each site to determine if reservoir criteria are met to drill a horizontal well. The input data varies for each area and is dependent on data availability.

Four directional well-site evaluations are presented to show the rationale behind the selection of the sites and how well design geometry is determined. Detailed analysis

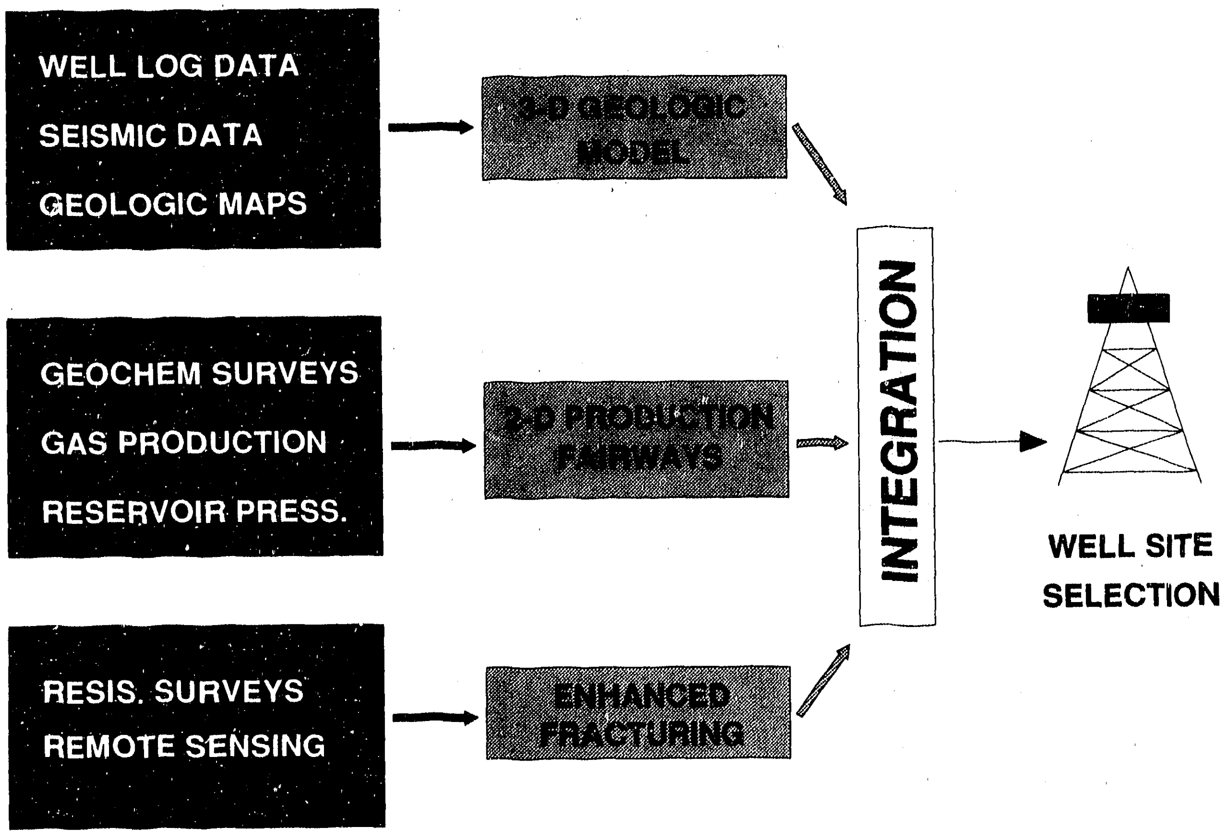

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Figure 1. Horizontal Well-Site Evaluation Flow Sheet

of well log data and surface geology are used to develop a three-dimensional model of the reservoir target. Seismic data is integrated, when available, to enhance detection of increased fracture porosity. The relationship of near-surface fracture trends to subsurface geologic structure is delineated using soil gas and water geochemistry and dual-depth resistivity surveys. The data are then integrated to form a reservoir model of the potential site and the basis for well design.

The four sites include the initial research well in Wayne County, West Virginia; a high-angle well project in Roane County, West Virginia; a horizontal well project in Putnam County, West Virginia; and the most recent site in Martin County, Kentucky. The Wayne County site was evaluated by BDM Corporation using well logs, geology maps, and seismic, resistivity, production, and pressure data. The Roane County site evaluation utilized well data, geology, and soil gas chemistry to define the fracture fairway and to locate and design the well. Putnam County was evaluated using similar data, plus water geochemistry, remote sensing, and shallow resistivity surveys. The Martin County site was selected by Columbia Gas, using production and pressure data, geologic interpretation of well log data, and remote sensing interpretation of side-looking airborn radar (SLAR) data. A geochemistry survey was run by METC personnel.

INTRODUCTION

The U.S. Department of Energy/ Morgantown Energy Technology Center (METC) has been active in drilling deviated Devonian shale wells in the Appalachian Basin for over 10 years. Wells have been drilled in Jackson, Wayne, Roane, and Putnam Counties, West Virginia, and in Meigs County, Ohio, to delineate the fractured reservoir and improve gas production economics from this tight formation (Figure 2). Early wells were designed to collect reservoir data on the distribution and geometry of the fracture systems in areas of established gas production. Results indicated the highly organic Devonian shale lithologies were the source and reservoir for most of the gas. Higher producing wells were located in areas where fracture density was increased because of geologic structure and in-situ stress conditions that kept the fractures open along mappable trends or "fairways."

There has always been difficulty in determining the shale characteristics that control the volume of gas production from individual wells in a proven field. The answer lies in a combination of geologic structure, in situ stress, and gas availability to the natural fracture system. This is especially true in horizontal wells, which attempt to maximize the number of fractures intersected over the length of the wellbore.

Criteria for horizontal well-site selection have developed over the years to include the assessment of a variety of exploration tools designed to aid in mapping enhanced fracture trends. Recent efforts utilize remote sensing, geophysical, and geochemical surveys to assist in determining subsurface fracture systems using near-surface measurements. The four horizontal well-site evaluations have shed some light on understanding the naturally fractured reservoir and developing a basis for siting horizontal wells in the Appalachian Basin.

WAYNE COUNTY, WEST VIRGINIA, RET NO. 1 WELL

The Recovery Efficiency Test (RET) No. 1 well was drilled by BDM Corporation as an initial research well to test the drilling

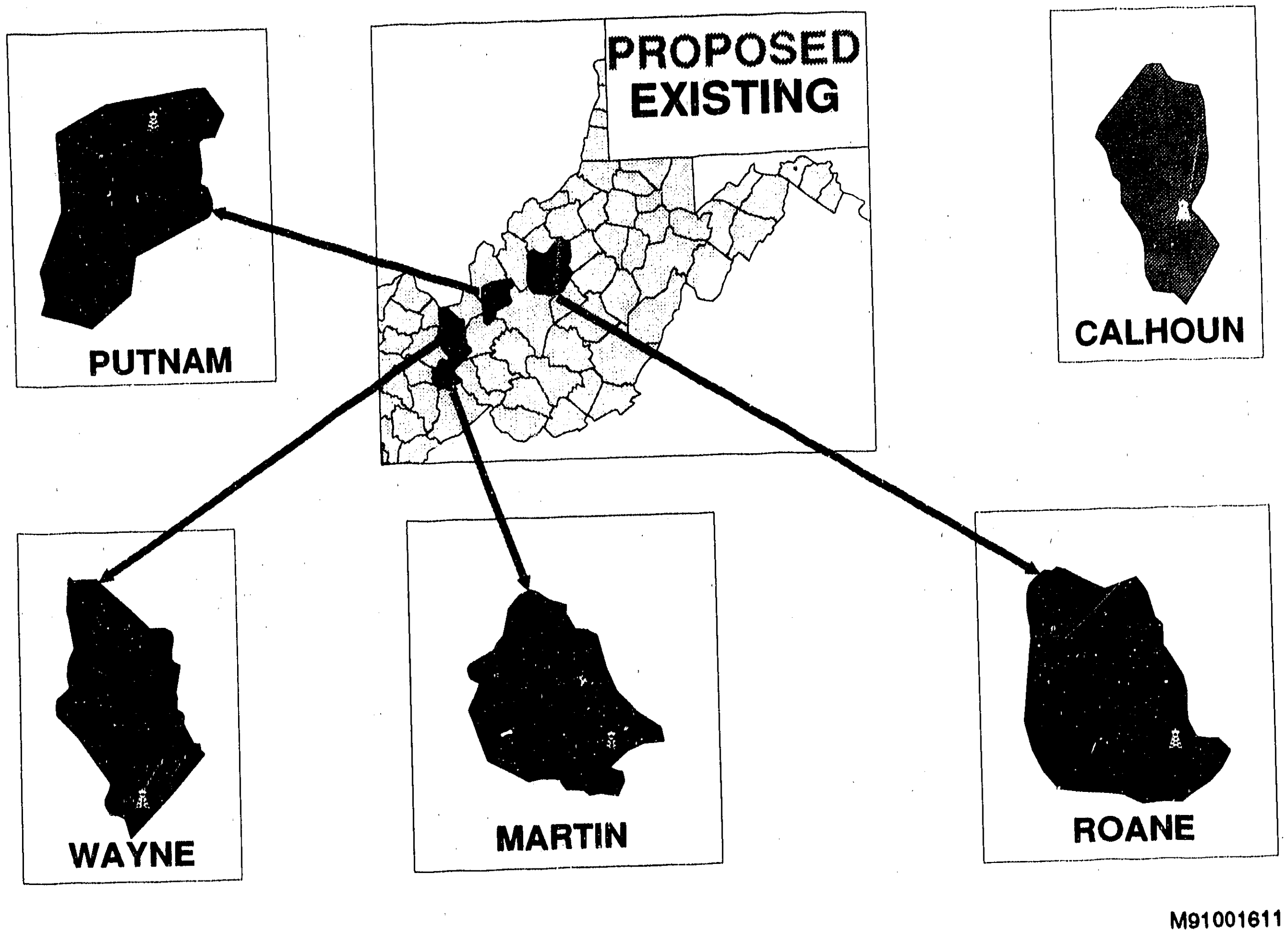

Figure 2. Horizontal Well Site Areas

technology in the shale reservoir (Figure 3). The site selection plan is used as the basis for future well site eva' ıations. A wide range of exploration tools v .re used to evaluate the project site to set the scope of work for future site evaluations. Detailed analyses of well logs, geological data, lineament interpretations, seismic data, shallow resistivity, geochemistry, and production data were completed for the area. These results were used to interpret the controls on gas production. Overall, the studies were successful in defining fracturing in the area and in the reservoir. The results were used to determine well location, wellbore direction, and subsurface geometry.

Structure: On the 1913 West Virginia geology map of Wayne County (Krebs and Teets), the well is located on the axis of a N-S anticline in the near-surface coalbeds. At the well location, the axis is striking N 35 to 40° W. The axes of the anticline and syncline to the east of the site indicate cross folding in the area. The Lower Huron shale structure map (Figure 4) essentially mimics the coal structure, showing the influence of cross folding by the offset of highs and lows with NE-SW and SE-NW linear features. The well is located on the transitional NE limb of the SE-NW anticlinal fold. An offset of approximately

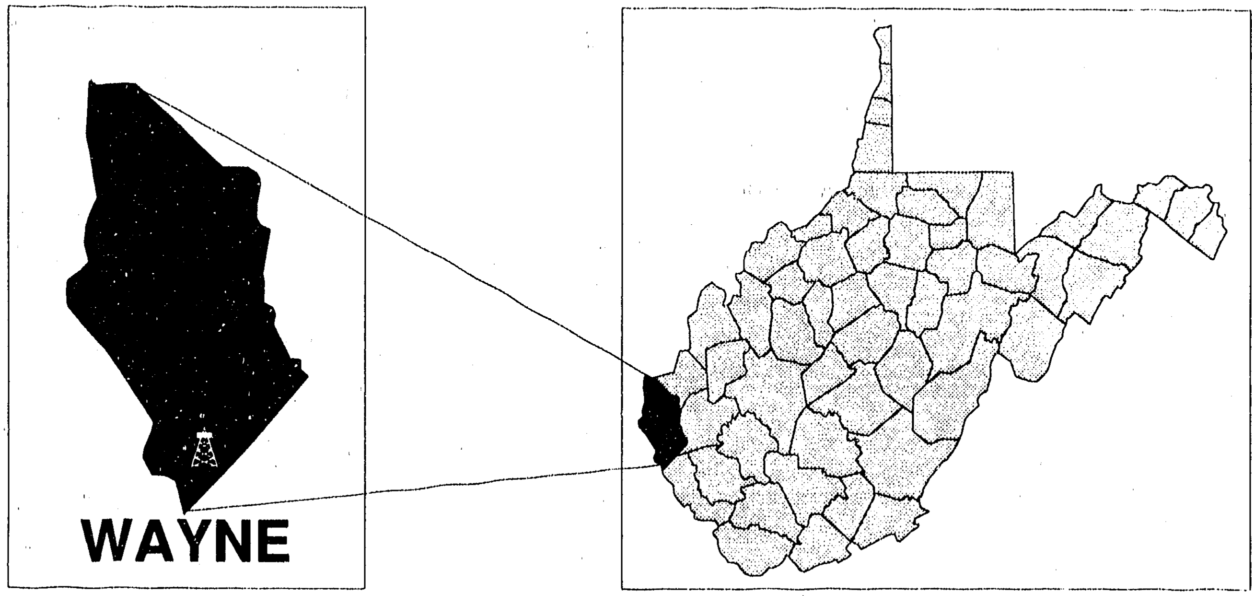

Figure 3. Wayne County Horizontal Well Site

1,500 feet occurs to the NE in the fold axis, evident when the structure on the coal and Lower Huron shale maps are compared. The offset indicates translational movement that probably occurred during compression and thrust faulting. The top of the Lower Huron is structurally more complex, showing effects of movement along the NE-SW linears. Neither of these orientations is associated with the major basement fault in this area, which strikes E-W. The dominant fracture trends in this area seem to be influenced by thin-skinned tectonics and cross-strike discontinuities when compared to production trends. Topographic linear trends indicate that the E-W and NE basement faults (Figure 4) may have been reactivated; however, they are not the primary open conduits controlling gas production.

Well Log Data: BDM Corporation used well logs to identify the Lower Huron target horizon and to quantify shale thickness. Cabot Oil and Gas contributed data for developing the maps. A large amount of data accumulated by GRI and Columbia Natural Resources in four quadrangles to the east of the site was used to help interpret the structure in the well site area. These two data sets were the main source of information for developing the geologic model and designing the well geometry. The data were confined to conventional logs, which were used to define formation tops and thicknesses; this information was used to construct structure and isopach maps of the shale intervals. Completion records were used to determine zones of maximum gas production in the formations. These zones are considered to be areas of open fractures in the shales and are best developed in the Lower Huron, which was the prime target of the horizontal section of the well. This was later substantiated with core from two zones in the well (Figure 5).

Resistivity Surveys: Mammoth Geo was contracted to run seven traverses of tri-potential resistivity in the well site area to

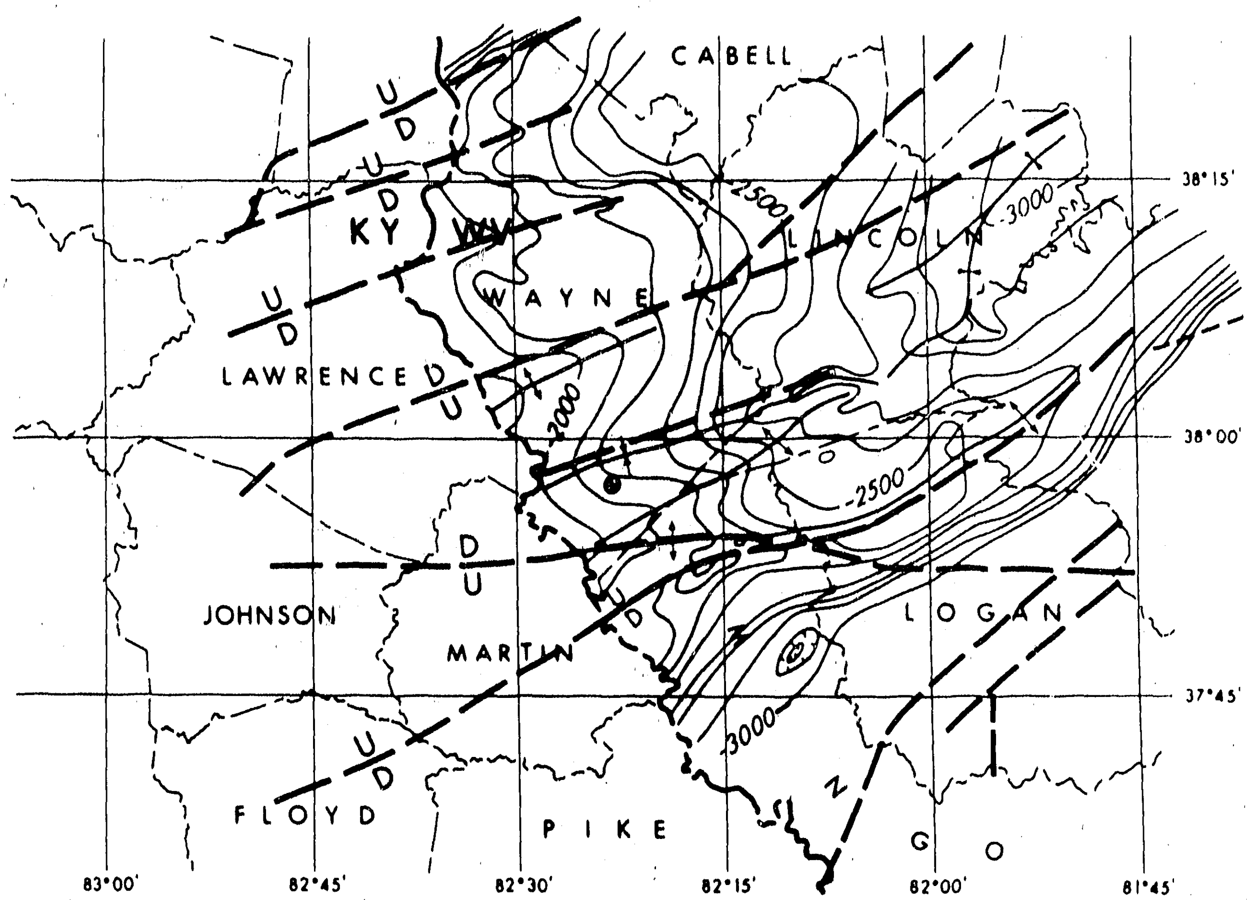

Figure 4. Structure Map on Top of the Lower Huron Shale, Wayne County Area (Contour Interval = 100 ft)

determine if anomalous zones of jointing could be detected using this technique. The dual-depth resistivity identified several zones of enhanced jointing in the shallow surface rocks. Two of these lines occur in the immediate vicinity of the well. The highly jointed anomalies detected at the surface correlate to a zone of fracturing in the horizontal section of the well just beyond the second cored interval. Other anomalous areas of increased jointing were mapped at the surface and correlate to fracture and production trends in the shales. The method is effective for ground truthing lineament locations in this area.

Production Trends: Analysis of production and pressure trends in the immediate well site area showed a strong SE-NW trend and a secondary SW-NE trend. The well was drilled S 45 E into a relatively undisturbed block, which was thought to have a rock pressure of 300 psi. The well was oriented perpendicular to the present day in-situ stress direction and secondary production trend. The orientation was based on all of the parameters and favored intercepting the highest formation pressures in the reservoir.

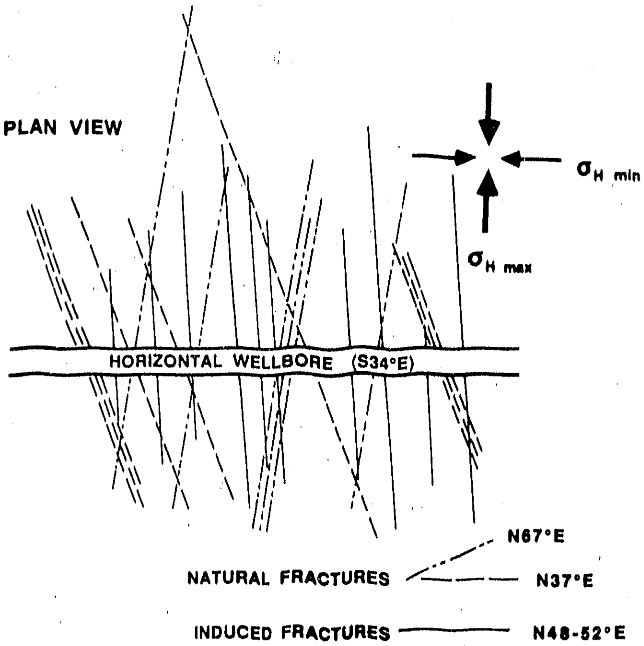

Figure 5. Fractures in the Lower Huron Shale, Wayne County Area

Directional Well Design: The final well geometry is shown in Figure 6 and was based on an evaluation of all the factors discussed in this paper. The well intercepted a number of fractures, indicated by visual inspection of two cores retrieved in the horizontal portion of the well, gas shows, and mud-log shows. An interpretation of video logging records shows areas of intense fracturing associated with the mud-log gas shows, indicating that the formation is fractured throughout the sampled interval.

ROANE COUNTY, WEST VIRGINIA, BOGGS NO. 1240 WELL

The Boggs No. 1240 well (Figure 7) was drilled in cooperation with Sterling Drilling and Production Company Inc., and Gas Research Institute in 1990 to test the potential for production enhancement using high-angle (greater than 60 degrees from vertical) drilling techniques. The original site selection plan included the review of completion reports, geologic maps, seismic sections, soil gas samples, well logs, and production data to create a three-dimensional model of the reservoir. Completion reports and geologic maps from the West Virginia Geologic and Economic Survey (WVGES) were used to develop a generalized structure map of the area (Hennen 1911; Sweeney 1986). Available public seismic data near the study area did not provide detailed information of any use to the study. Therefore, primary site evaluation inputs were completion data, soil geochemistry, well logs (including electric, driller's, mud, and borehole video), and production data.

Structure: Geologic structure in the area is dominated by a NE-SW trend as indicated by fold axes. The folding essentially follows the strike of Pre-Cambrian basement faults, but is offset by cross-strike discontinuities (CSDs). The CSDs are related to thin-skinned tectonics (Gwinn 1964) of the Allegheny Orogeny and affect other geologic features. The actual study area lies on the west flank of the Chestnut Ridge Anticline, sharing a common limb with the Robinson Run Syncline to the west. The Burning Springs Anticline lies NW of the field in northern Calhoun County, a structure developed from thrust faulting along a decollement plane in the Salina salts (Sweeney 1986).

Well Log Data: Well log information was collected from the WVGES and gas companies active in the area. Earlier studies by Gas Research Institute (GRI) added information to the data set used to evaluate geologic structure and gas production (Lowry et al. 1989).

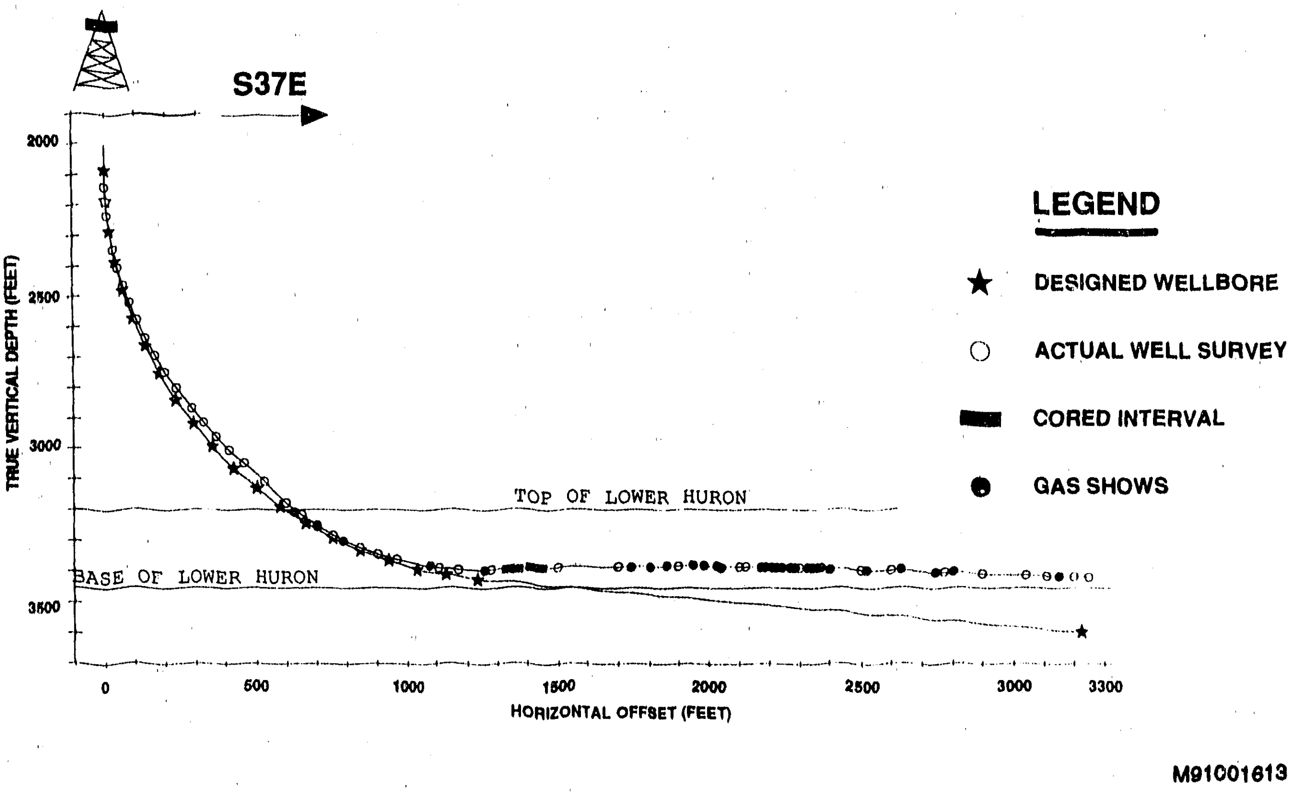

Figure 6. Cross-Section S 37° E for RET No. 1 Horizontal Well

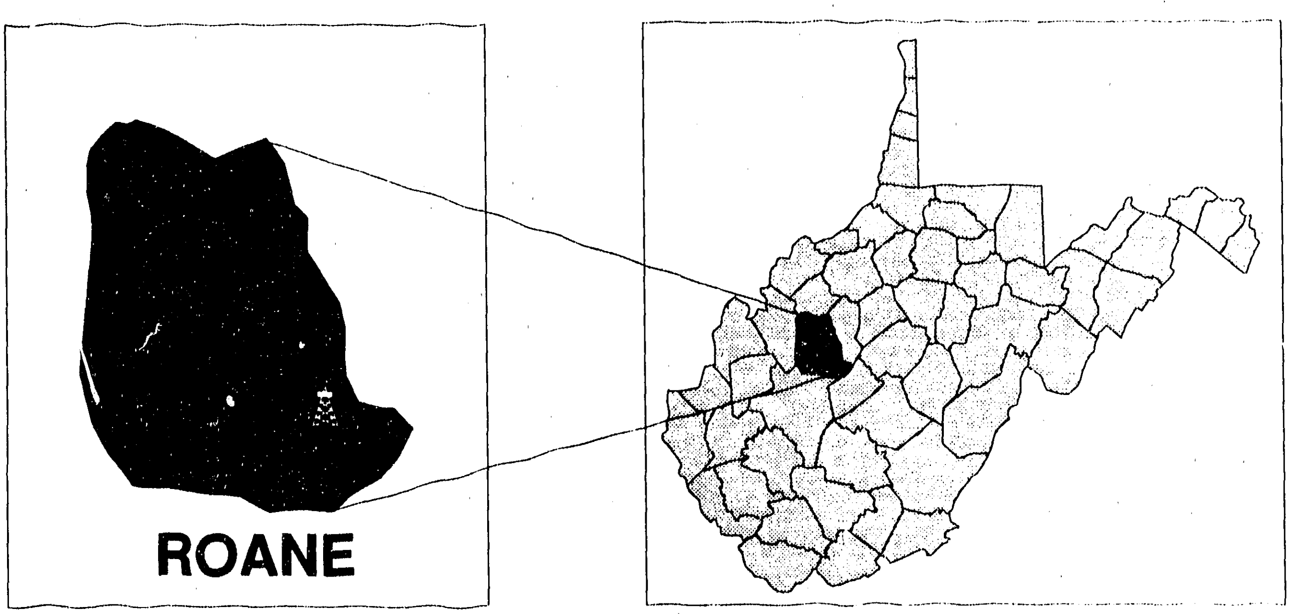

Figure 7. Roane County High-Angle Well Site

Structure within the Beech Fork field was determined from open-hole electric logs on 35 wells and from driller's picks as recorded on well completion reports from approximately 50 surrounding wells. Driller's picks were limited to the top of the Berea Sandstone overlying the Devonian shale sequence, since individual shale formation tops were rarely reported. Electric open-hole well-log formation tops were determined based on Gamma Ray and changes in shale bulk density.

Structure on top of the Berea Sandstone (Figure 8) indicates a NW dip to the axis of the Robinson Run Syncline. A reverse fault

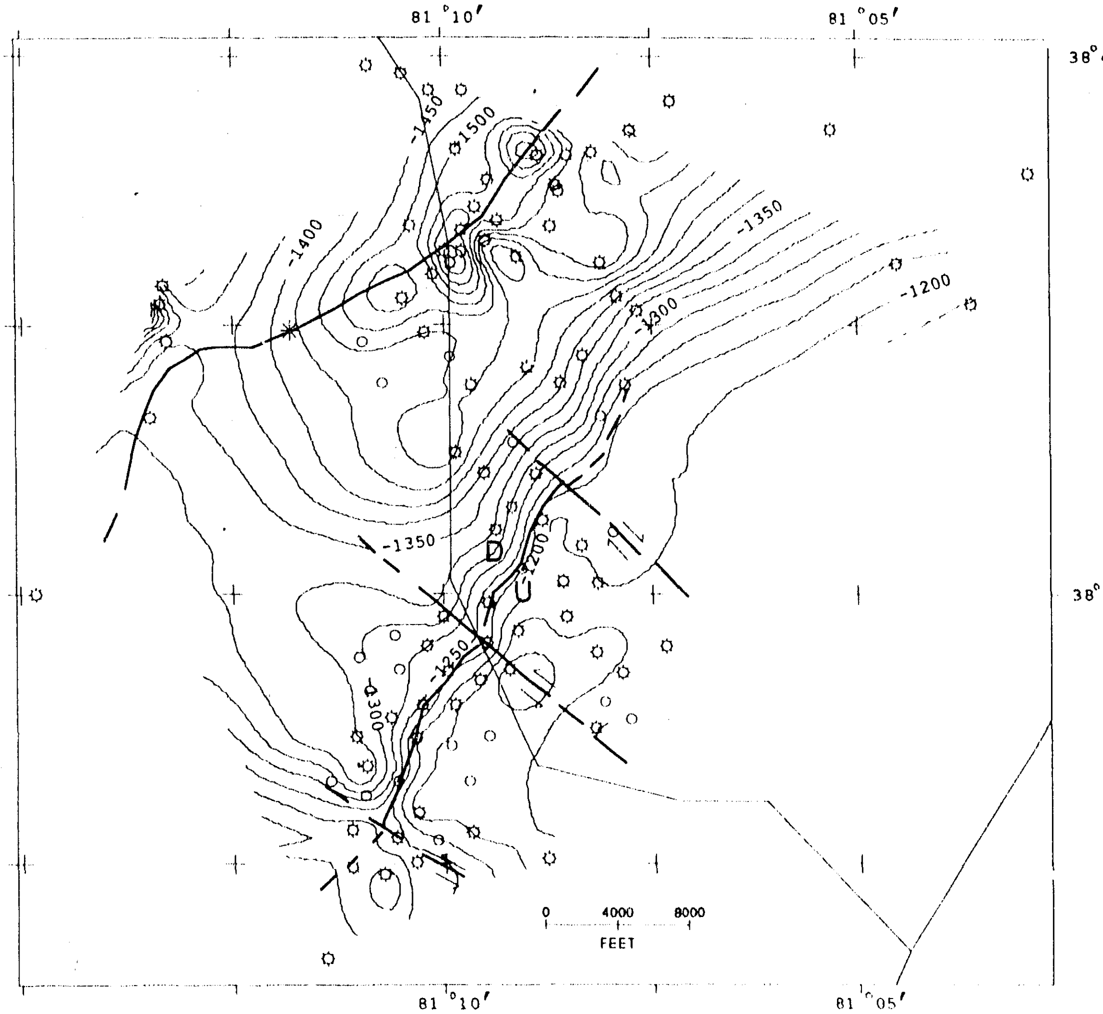

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Figure 8. Structure Map on the Top of the Berea Sandstone, Roane County Area (Contour Interval = 25 ft)

oriented N 25° E traverses the center of the study area, creating a slight monoclinal roll and thickening along the limb of the anticline. Lowry and Peterson (1988) suggested the reverse fault could be the high-angle section of a thrust fault originating in the Middle-Lower Devonian or Upper Silurian. Reeves (T.K. Reeves, 1988, R. T. Associates, Canonsburg, Pennsylvania, Personal communication) theorized the reverse fault may be related to basement faulting associated with the Rome Trough.

A NW-SE cross-strike discontinuity (CSD) crosses the center of the study area. The CSD postdated the reverse fault, since a slight shifting of the reverse fault to the NW is evident north of the CSD. Hennen (1911) also reported an offset in the Robinson Run synclinal axis in a NW direction, directly in line with the trend of the CSD. The northern end of the Tariff oil field, which produces from the stratigraphically higher Big Injun Sandstone, also terminates against this CSD. A major surface lineament and higher production trends also aline with this CSD.

Examination of open-hole logs indicated the presence of fault-induced bed duplication and thickening in several wells north of the major CSD. Similar bed thickening and repetition were reported by Lowry (1988) as part of a GRI study of the area. A highly fractured area lies north of the CSD and correlates well with the bend in the Robinson Run synclinal axis (Hennen 1911). Movement along the CSD apparently created a shear zone at the pivot point. Thrust faulting occurred within the shear zone, resulting in bed thickening and duplication of units.

A smaller CSD or shear zone lies to the south of the major CSD. The extent of this fracture zone west of the reverse fault could not be determined because of a lack of well data. However, Hennen (1911) did not indicate any corresponding offset in the Robinson Run synclinal axis.

Similar structure is seen on top of the Lower Huron shale (Figure 9). The extent of and any offset in the southern CSD again could not be determined because of a lack of well data. Thickening of the shale unit north of the major CSD is evident on the Lower Huron isopach (Figure 10). A block diagram representing the interpreted three-dimensional geology on top of the Lower Huron shale is shown in Figure 11.

Soil Geochemistry: An effort was made to map production trends in this area using shallow soil gas sampling. The results were not conclusive for a number of environmental reasons. Soil conditions were very dry with no moisture in the upper 1 m (3 ft) of the section. The wells in the area have been in production for 3 to 5 years and may have depleted the migration mechanism, causing the negative anomaly over the production trend (Figure 12). Contamination caused by historic gas and oil production in the area may have masked some of the subtle features or trends that existed in an undisturbed condition. Overall, the survey showed past and present drilling activity in the area, not geologic structure. Because of the low values of gases analyzed, it would be inappropriate to correlate the survey results quantitatively.

Production Trends: Initial open flow after stimulation (IOFA) and the first 12 months of cumulative production were evaluated to determine if any production trends existed within the Roane County study area (Figures 13 and 14). An arbitrary IOFA value of 500 Mscf/d was selected as the criteria to determine a good well in the area. A SW to NE oriented production-trend "fairway"

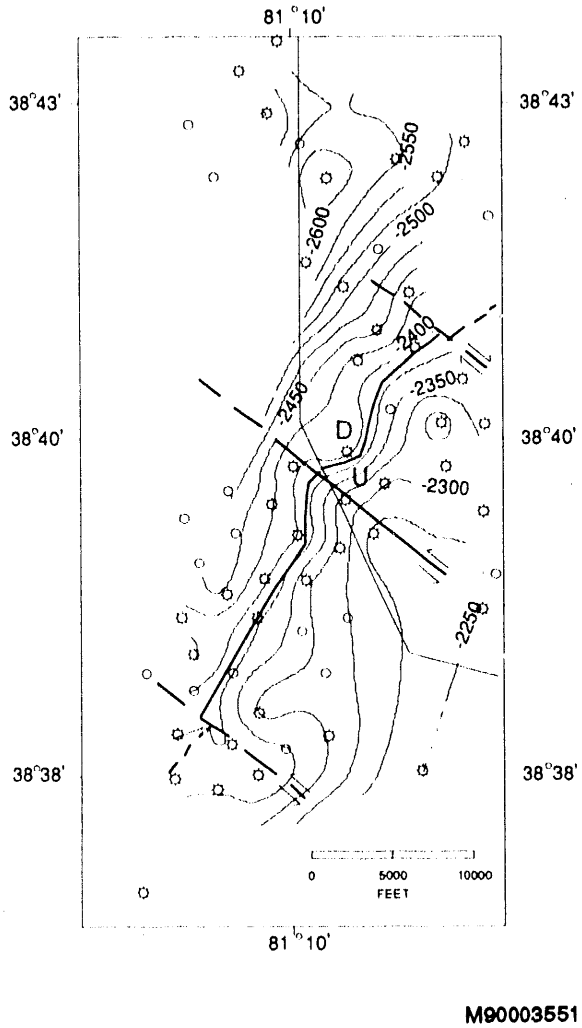

Figure 9. Structure Map on Top of the Lower Huron Shale, Roane County Area

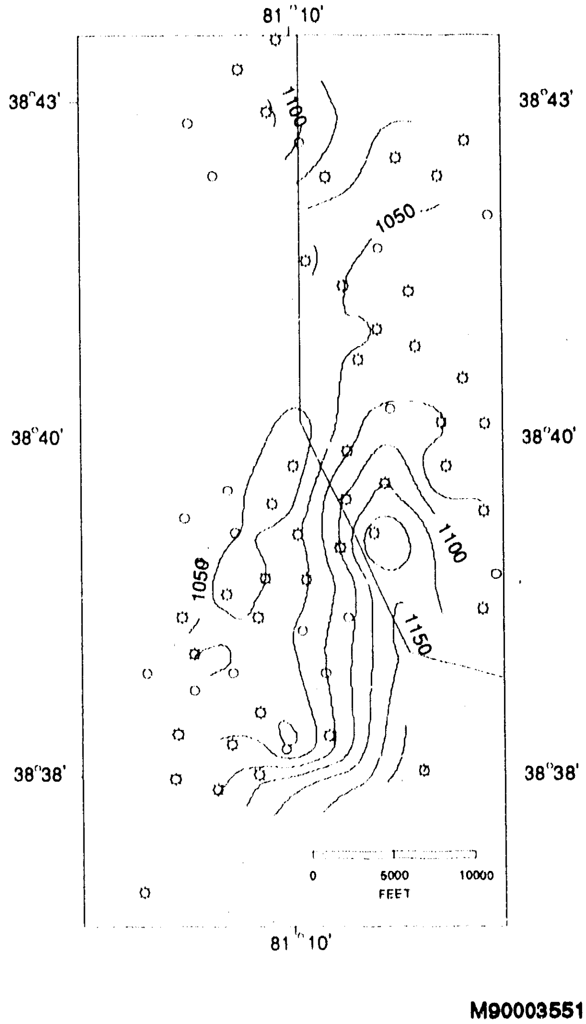

Figure 10. Isopach Map of the Lower Huron Shale, Roane County Area

was found to exist across the field (Figure 13). This trend directly overlies the NE trend of the reverse fault zone through the field. The highest open flows (greater than 2,000 Mscf/d) were evident at the intersection of the reverse fault zone and the major CSD.

Mapping 12-month cumulative production from each well indicated a similar trend (Figure 14). Twelve-month production in excess of 100 MMscf was evident at the intersection of the reverse fault zone and the major CSD. Higher yields were also evident associated with the shear zone to the north and, to a lesser extent, the zone to the south of the major CSD. Production on either side of the faulted (fractured) zones appears to be the natural contribution of the Devonian shales and siltstones within the area. Without the increased natural fracturing

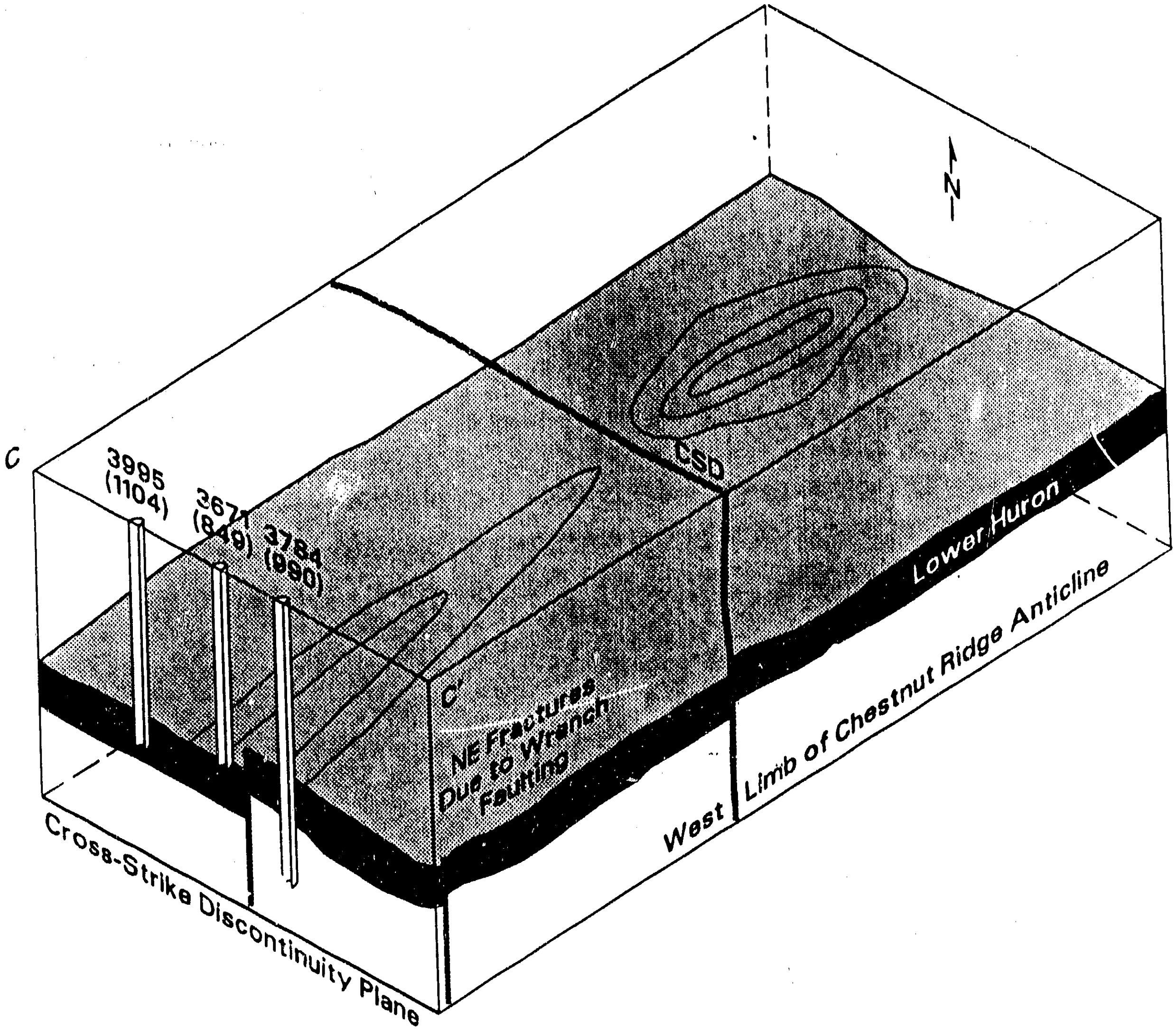

Figure 11. Block Diagram of Geology on Top of the Lower Huron Shale, Roane County Area

associated with the faulted (fractured) zones, yields of less than 25 MMscf (and in many cases less than 10 MMscf) were evident for the first 12 months of production.

Directional Well Design: Analysis of open-hole noise and temperature logs, cased-hole production logs, and down-hole video surveys indicated the producing reservoir was limited to a few multiple entry point sources of gas over a relatively limited vertical extent of wellbore. The well was designed to cross numerous natural fracture zones by entering the top of the fractured target from the NW, slanting across the target, and exiting the base of the target to the SE. The planned wellbore design and an actual drilled well schematic are shown in Figure 15. Location of the high-angle well with respect to production is shown on Figure 14.

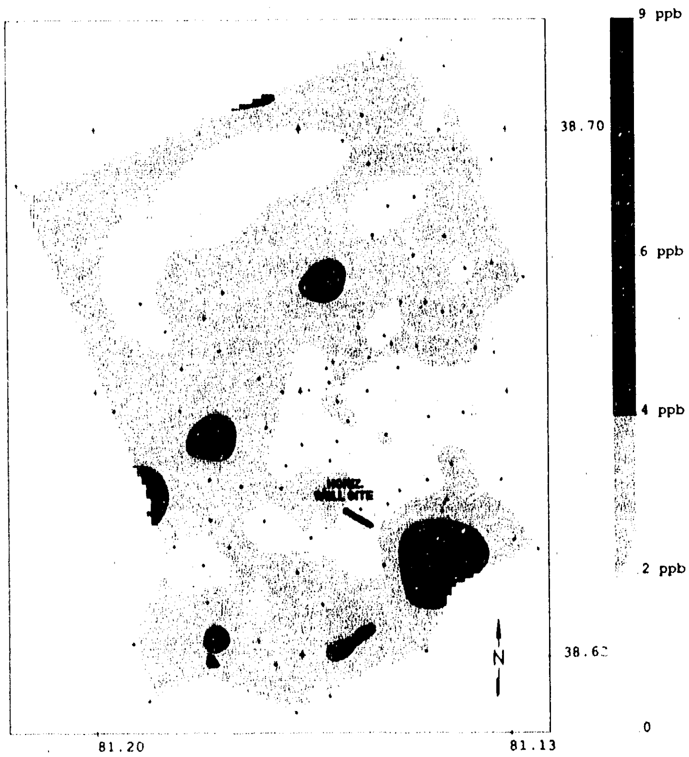

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Figure 12. Map of Soil Methane, Roane County Area

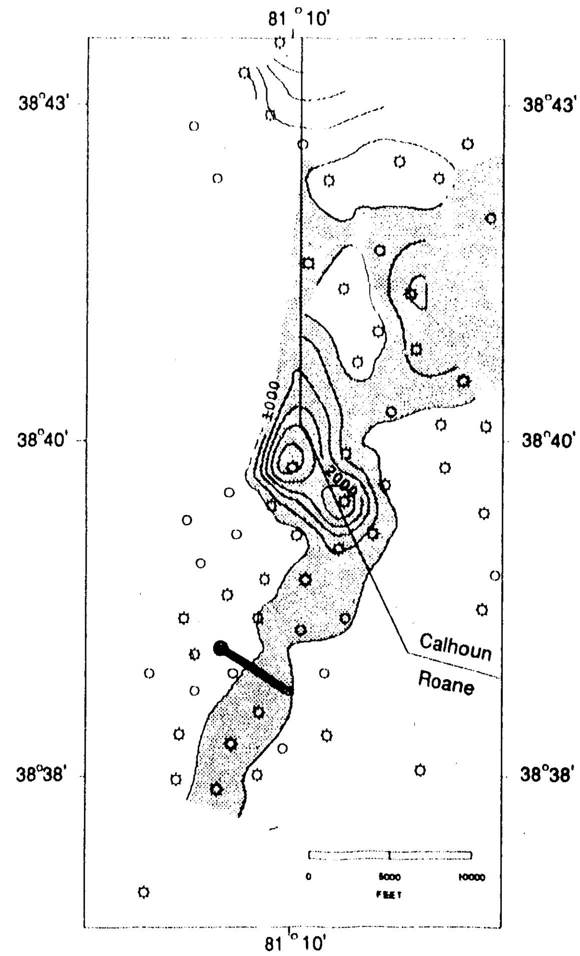

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Figure 13. Initial Open Flow After Stimulation, Roane County Study Area

PUTNAM COUNTY, WEST VIRGINIA, HARDY HW NO. 1 WELL

The Hardy HW No. 1 well (Figure 16) was drilled in cooperation with Cabot Oil and Gas Company and BDM Corporation. The data set for this well site varied slightly from the Roane County data set, as did the geologic setting. Two more surface exploration tools were used to determine their viability.

Structure: The northern part of Putnam County has historic production from the Devonian shale interval in the Midway-Extra field. The horizontal well site is located along the NE extension of the field near the Jackson County line. Production is associated with a structural roll or monocline in the shale, overlying a basement fault where fracturing is more intense, resulting in increased permeability. The strong NE trend is modified by N-S basement faults that terminate the production at random intervals along strike.

The county geological report and map indicate a number of other features related to basement fault involvement (Krebs 1911). Fold axes are parallel to basement faults and are offset by NW CSDs. The near-surface

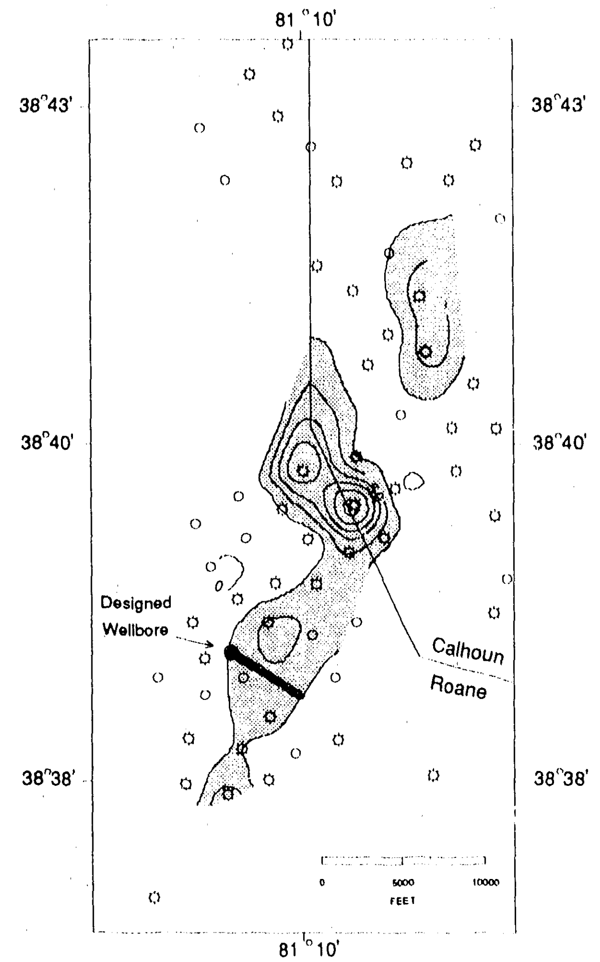

Figure 14. First 12 Months of Production, Roane County Study Area

coals show strike-dip and depositional geometries affected by NE and N-S fault trends. Studies by Shumaker (1981) showed that deep faulting controlled the shale structure within the area.

Well Log Data: Structure and isopach maps were created from well data to evaluate trends associated with production (Figure 17). The eastern trends in the deeper Oriskany Sandstone showed strong correlations to N-S basement faulting, which controlled sand deposition. The western Devonian shale trend is productive on a SW-NE trend over a basement fault, which is terminated by N-S faulting.

Remote Sensing: A remote sensing study was run as part of the site evaluation effort. The analysis uses an algorithm to select linear features from the U.S. Geological Survey digital elevation model (DEM) data at a 7.5-minute scale. Linear features were mapped in three dimensions as vectors and then were compared to create three-dimensional planes. Dominant plane sets were mapped in three dimensions and were compared to surface and subsurface geologic structure. Plane sets mapped on this site correlated to subsurface expressions of basement faults, indicating reactivation of faults and enhanced fracturing along these features. The remote sensing study showed that in conjunction with well data and geology, this can be a viable tool for mapping enhanced fracturing in a basin.

Soil Geochemistry: Soil gas and well water geochemistry surveys were conducted in the vicinity of the well site. The soil geochemistry survey was not conclusive because of poor soil conditions. Prior to the sampling, heavy rains and saturated soil conditions along with calcareous, clay-rich lithologies made it impossible to obtain gas from these "plastic-like" sediments. Samples retrieved indicate the distribution of soil types, not enhanced gas-migration geologic structures. The few positive gas anomalies, however, occur over major lineaments associated with the subsurface geology.

Water well analyses were conducted using methods described by Jones and Rauch (1978). High-bicarbonate ion concentrations correlate to an increase in gas productivity in shale wells. High-bicarbonate ion concentrations were found

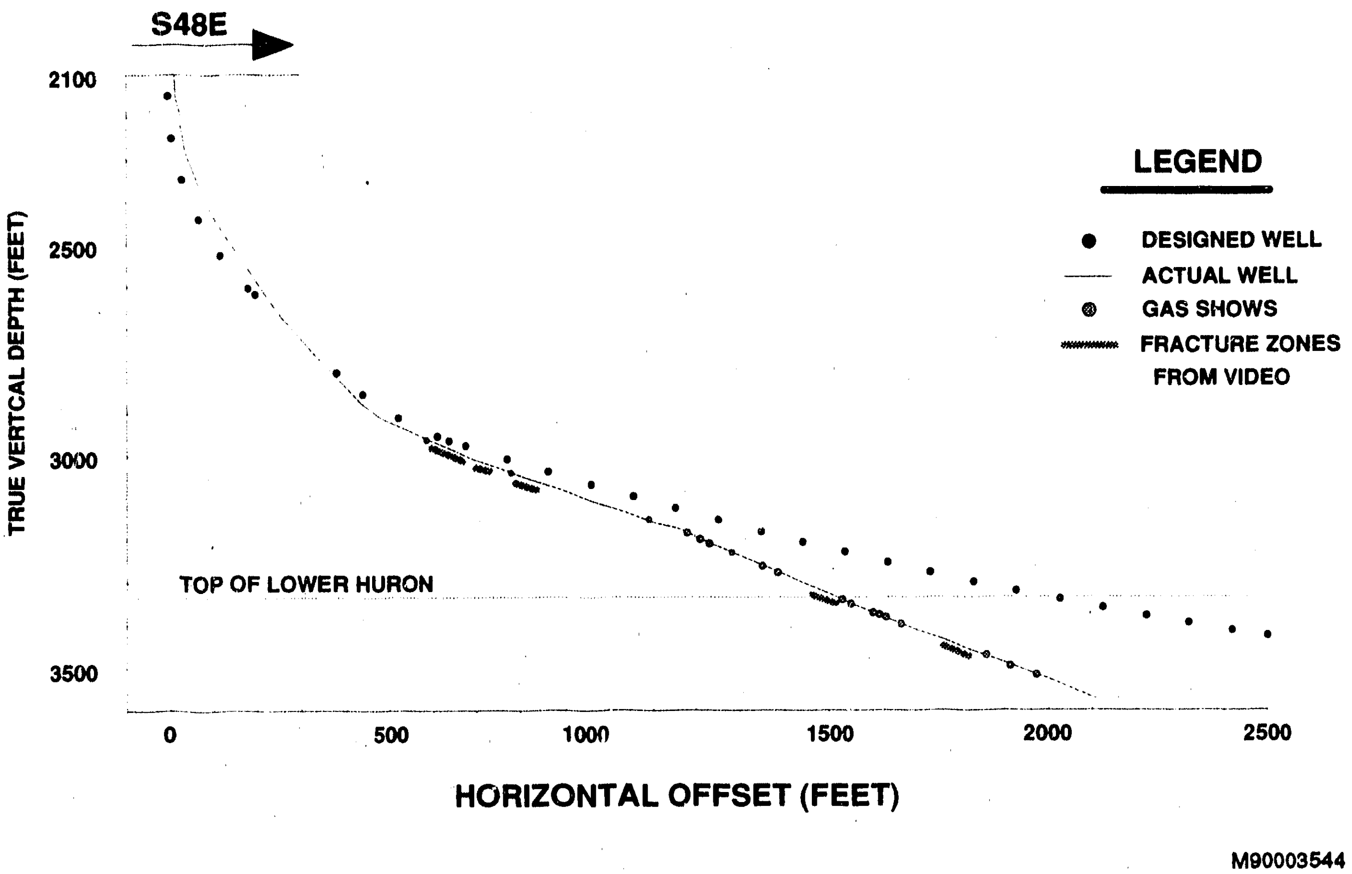

Figure 15. Cross-Section S 48° E for Boggs No. 1240 High-Angle Well

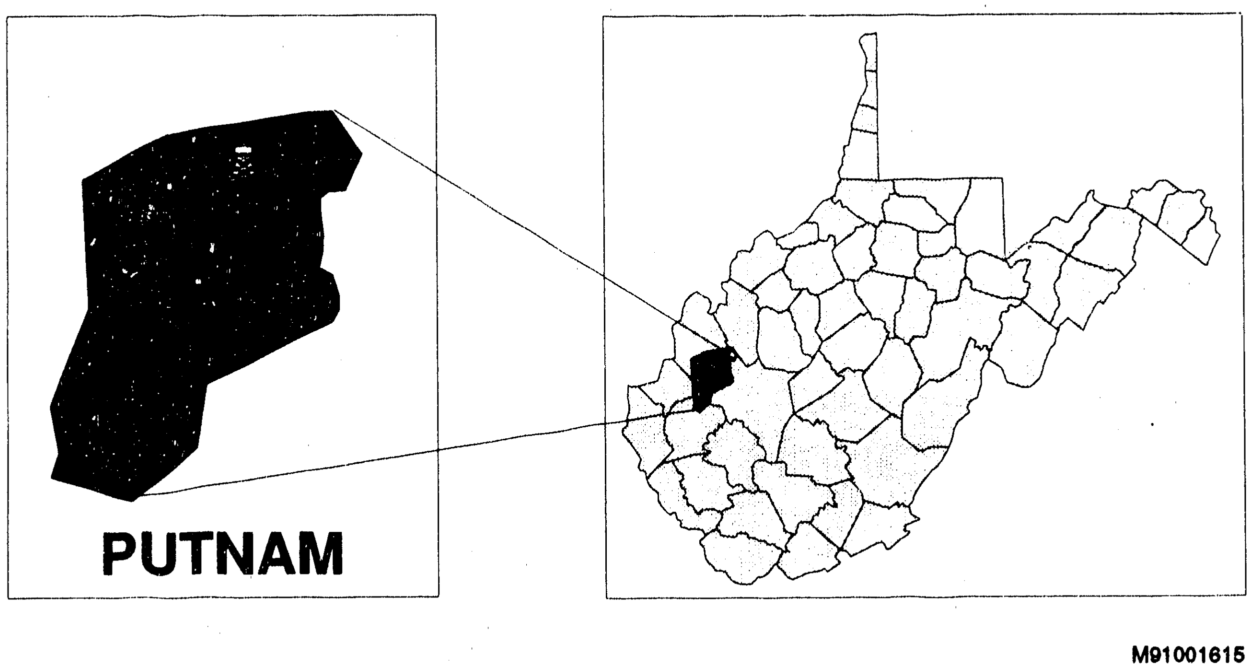

Figure 16. Putnam County Horizontal Well Site

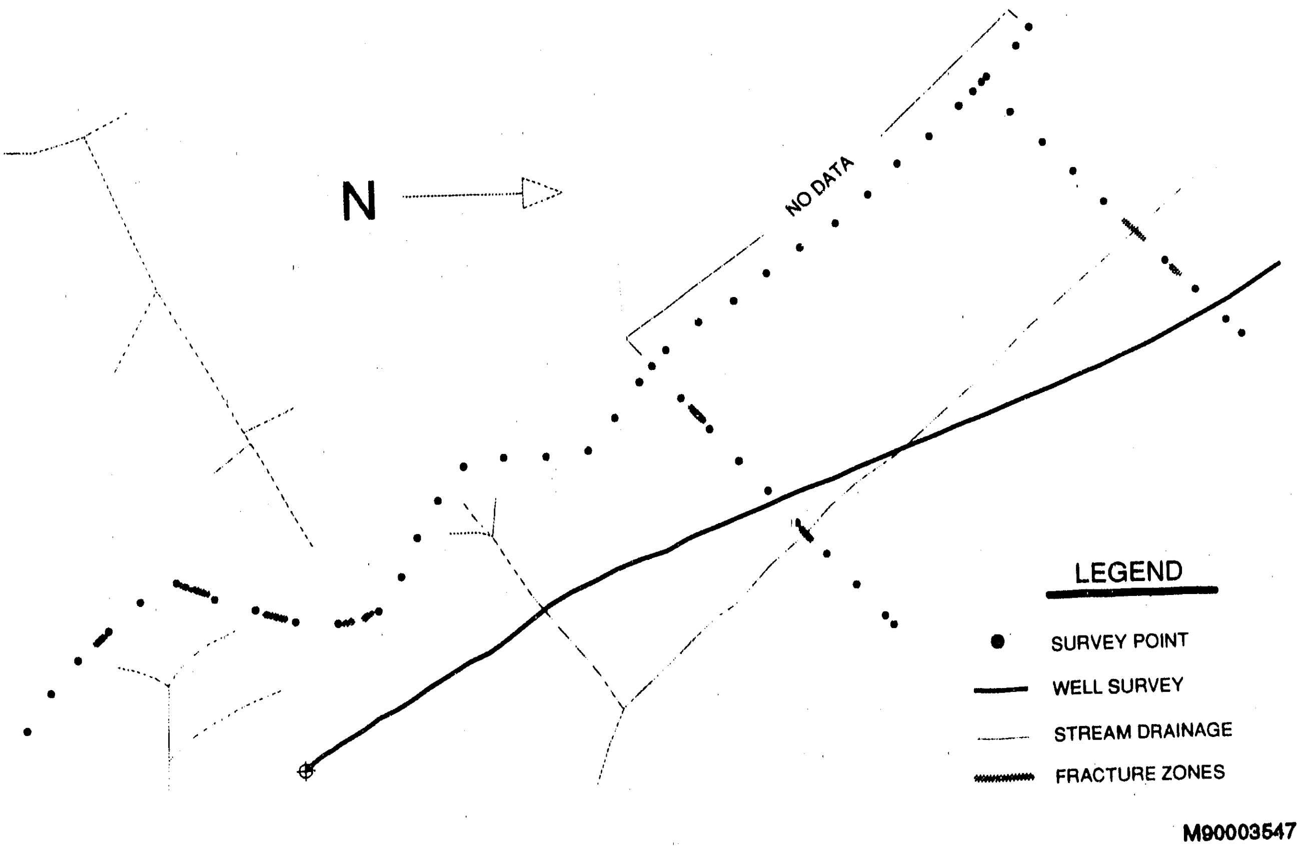

Figure 17. Structure Map on the Top of the Lower Huron Shale, Putnam County Area

near the well site, indicating the potential for a successful well.

Resistivity Surveys: A dual-depth (17 and 35 m [50 and 100 ft]) resistivity survey was run parallel to the length of the horizontal well to determine joint spacing and near-surface intensity. The first 760 m (2,500 ft) indicated several joint sets coincident with valleys and ridge top saddles (Figure 18). The dominant joint set correlates to the NE trend of valleys that parallel the strike of surface geologic structures and basement faults. The last 300 m (1,000 ft) were complicated by an induced ground current, caused by either a buried telephone cable or a poorly insulated electric fence. Therefore, correlation of surface joint spacing to subsurface fracturing with respect to the horizontal portion of the well could not be determined.

Seismic Studies: Several seismic sections have been run across the study area. All lines showed significant basement faulting and associated deformation of the overlying Paleozoic rock. The seismic surveys tend to substantiate the structure in the area as determined from well log analyses.

Production Trends: Structure controls the distribution of oil and gas in this area. A comparison of production to structure indicated oil was associated with down-thrown grabens. The best gas wells were associated with structural highs in the shale and the

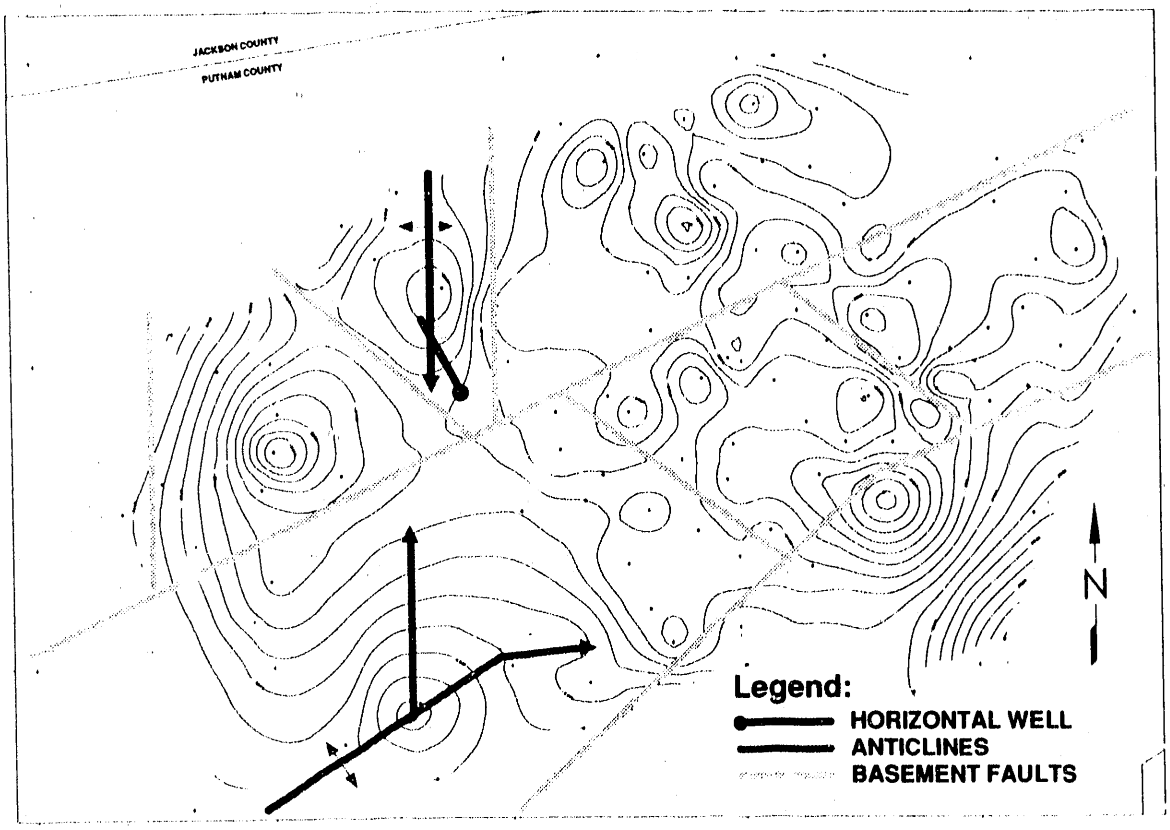

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Figure 18. Resistivity Study, Hardy HW No. 1 Well

greatest slope changes. Production, initial rock pressures, and initial open flow data showed a strong correlation to enhanced fracturing caused by reactivation of basement faults. Figure 19 shows the final well geometry with respect to design. The horizontal section of the well was planned to intercept the slope of an up-thrown block where fractures are open. The distribution of mud gas shows indicates at least ten fracture zones were intersected, with most of the gas coming from two highly fractured areas.

Directional Well Design: The well was designed to intercept an area where the structural slope change was the greatest on an up-thrown block. The block was bounded to the east, south, and west by basement faulting (refer to Figure 18). The planned design and actual well path are shown in Figure 19.

MARTIN COUNTY, KENTUCKY, COLUMBIA NO. C21747 WELL

The most recent well was completed in northeast Martin County, Kentucky (Figure 20), in cooperation with Columbia Natural Resources (CNR). CNR's staff accomplished the majority of the site evaluation effort using proprietary data that included well logs, SLAR data, production and pressure data, and completion reports.

Structure: Structure and isopach maps show several anomalous features in the well site area. A change in strike in the shale structure shows a N-S trend in the western part, changing to a NE strike in the northeast into the proposed well site. A change in dip is also noted in the area, which usually

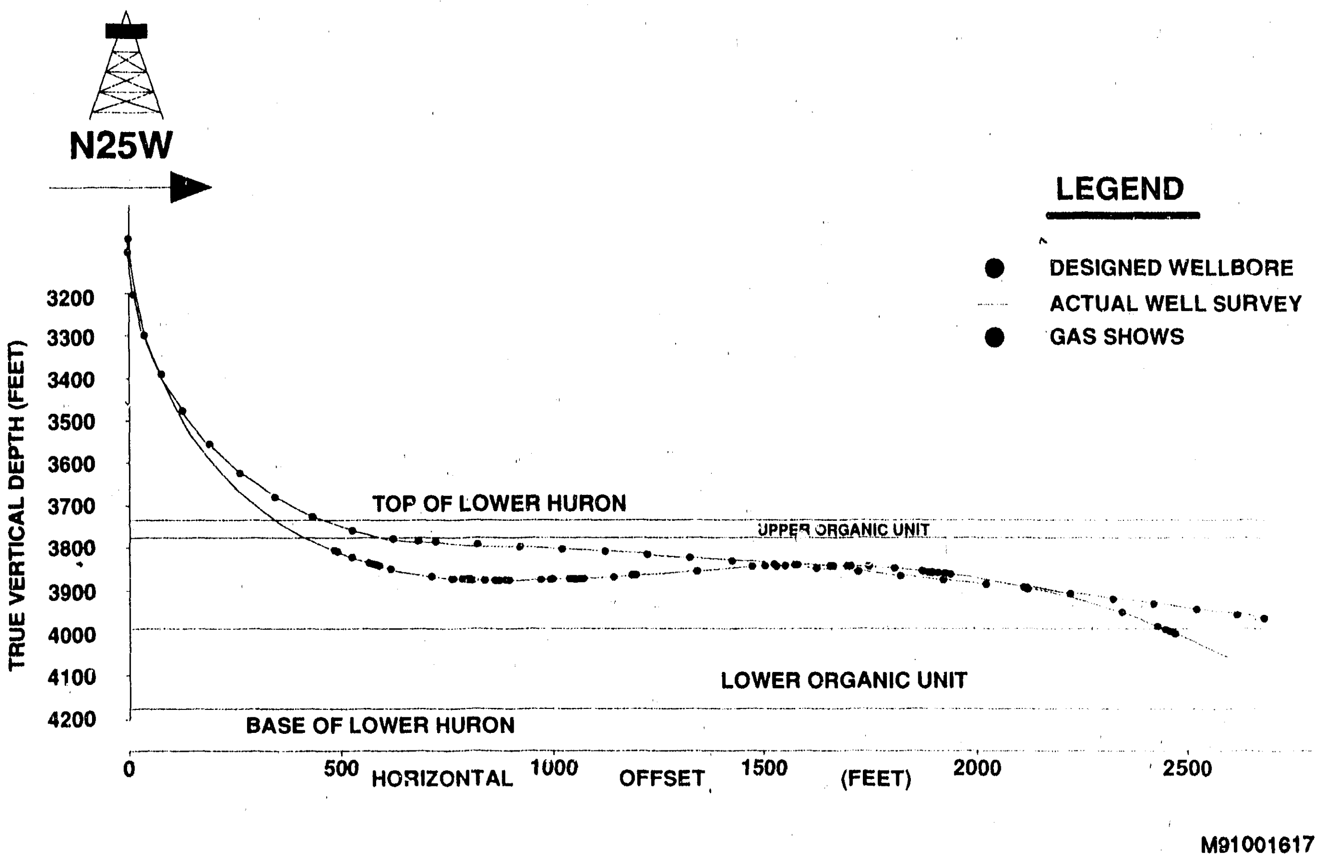

Figure 19. Cross-Section N 25° W for Hardy HW No. 1 Horizontal Well

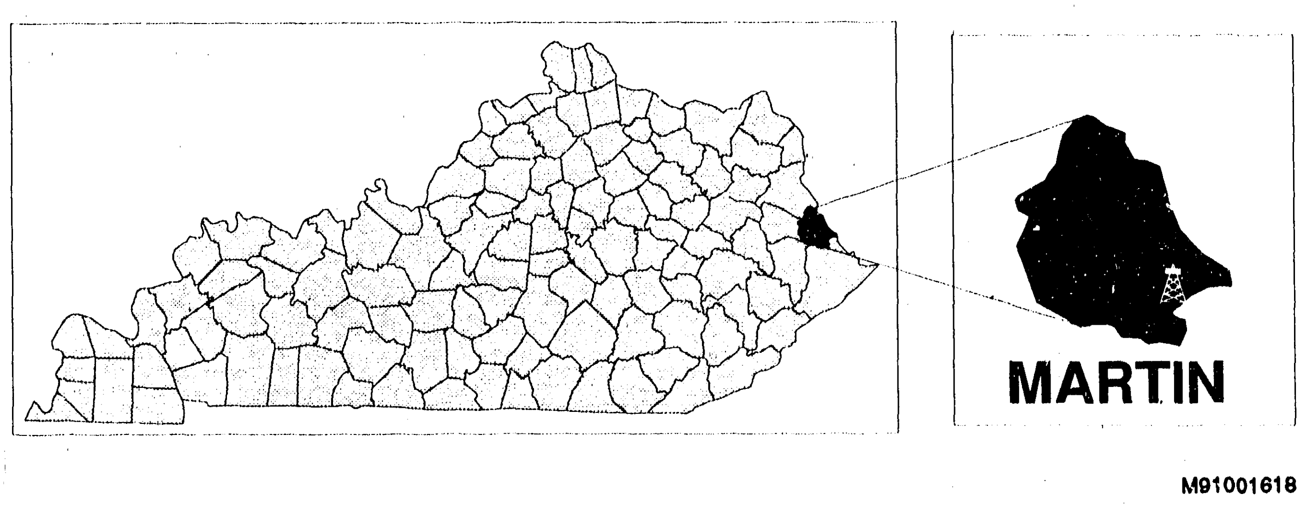

Figure 20. Martin County Horizontal Well Site

correlates to deeper basement faulting and enhanced fracture porosity. Production trends in the shale support this interpretation. The isopach map shows an increase in shale thickness to the east. The rate of thickening changes at the N-S fault on the structure map. This is an apparent hinge line feature associated with basement fault movement. The well was located on top of the NE fault trend, which may have been detrimental to drilling through the most highly fractured zone. The design causes an offset of at least 600 feet NW of the prime target fairway.

Well Log Data: Structure and initial rock pressure maps were generated of the Lower Huron shale reservoir (Figures 21 and 22); a cross-section based on well logs was also generated to delineate the target horizon. This information, in conjunction with completion reports, identified the Lower Huron shale interval as the most fractured, gas-producing horizon.

Soil Geochemistry: A soil gas geochemistry survey was completed in the study area with mixed results. An attempt was made to sample several topographic lineaments identified in the SLAR analysis. Only two high values occur in the data and neither have been successfully correlated to structure. The overall values for C1-C7 hydrocarbons is low, as was found in other areas of extensive drilling and historic production. The explanation for the low values is reduced formation pressure driving the gas that is

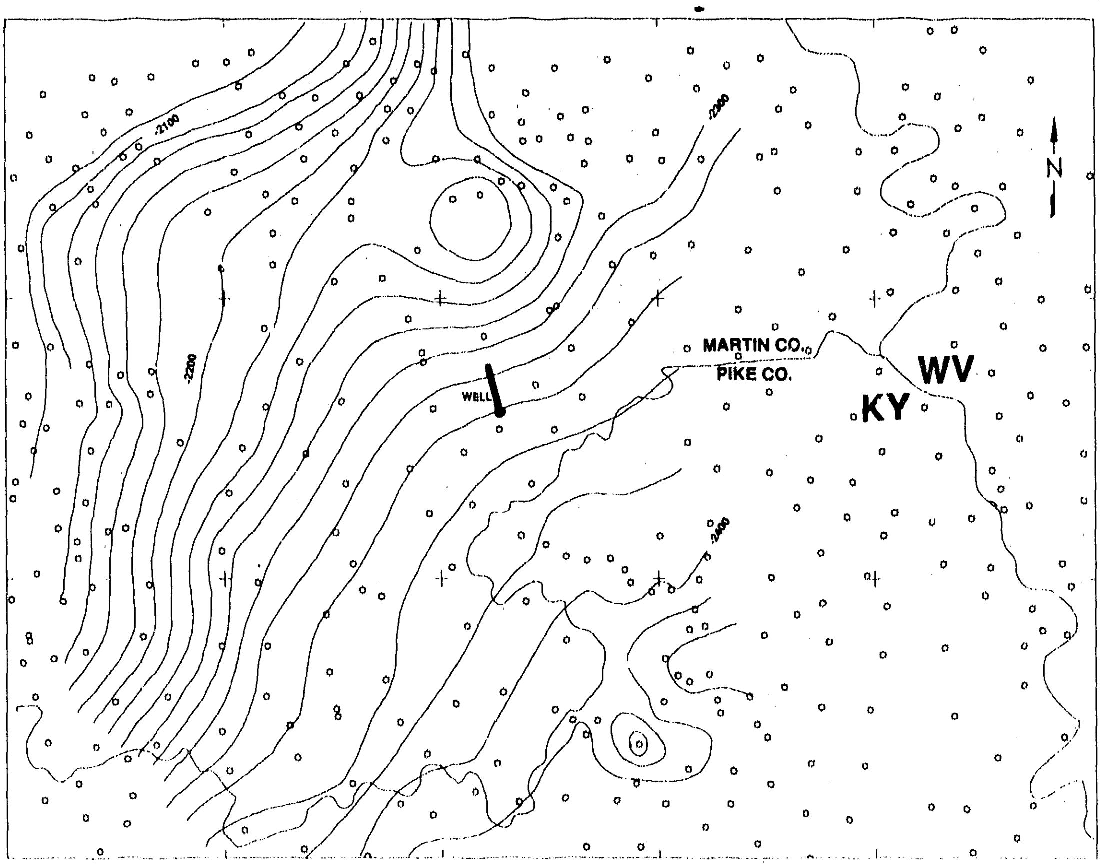

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Figure 21. Structure Map on Top of the Lower Huron Shale, Martin County Area (Contour Interval = 20 ft)

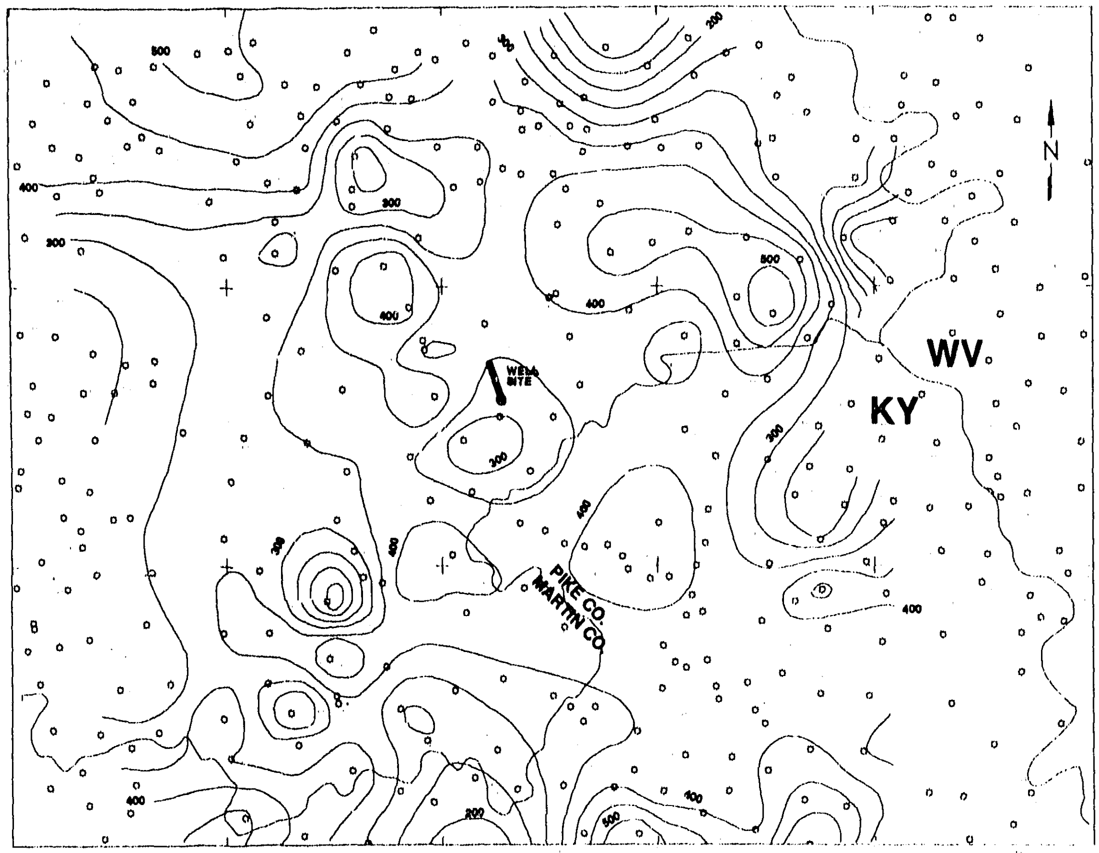

Figure 22. Map of Initial Rock Pressure, Martin County Area (Contour Interval = 50 psi)

migrating to the surface. The stratigraphic column contains coal beds; this complicates the interpretation because coals can trap gas and also be a source of methane. The soil conditions in the area were conducive to sampling, but consisted of sand, which can vary in gas content depending on moisture conditions. Moisture conditions varied considerably from valley bottoms to ridge tops, which added another variable to further confuse data interpretation.

Production Trends: Production fairways and pressure distribution in the shales were used to locate several potential sites. The production trends followed some of the lineaments identified in the SLAR analysis. High-production areas also confirmed the two anomalies noted on the structure and isopach maps. The strong NE fairway was selected, based on the parameters discussed. This fairway was successful in intercepting a number of fracture systems and significant production. Figure 23 shows the well configuration and distribution of gas and fractures in the horizontal section.

CONCLUSIONS

Shale gas in the Appalachian Basin is profusely distributed across the western portion, and is enhanced where the source shale is fractured mainly through the reactivation of basement faults. This reactivation, caused by uplift and erosion of the

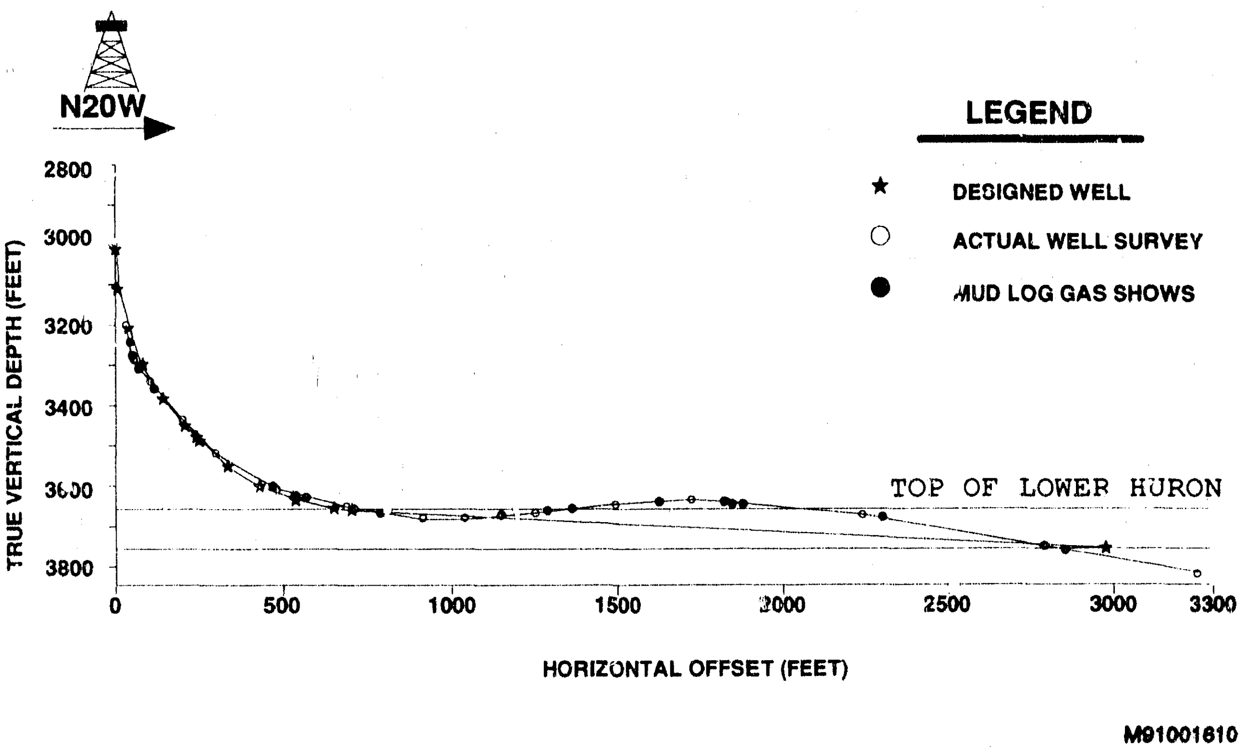

Figure 23. Cross-Section N 20° W for Columbia No. C21747 Horizontal Well

overlying Paleozoic sediments, has overprinted earlier tectonic structures and can be mapped with various exploration tools.

The application of soil gas sampling was found to be a difficult task in the basin environment because of several geologic and environmental problems. The lithologies found at the surface became impossible to sample in very dry or very wet conditions. The amount of contamination from earlier oil and gas production can mask subtle anomalies, and present production can erase them altogether.

From the one study area tested, ground water geochemistry does appear to have some merit as an exploration tool. However, additional testing is required to determine the procedure's actual validity.

Resistivity surveys confirmed near-surface features associated with topographic features. However, near-surface metal and electric interferences can mask or eliminate detection of enhanced fracture porosity at the reservoir level.

State survey well-log data, producers' production and reservoir pressure data, geologic maps, commercially available seismic data, and remote sensing studies can be used to map enhanced fracture fairways in the Devonian shale reservoirs. The information must be integrated to build a three-dimensional model of the area to understand the relationship of the geology to the distribution of gas. With this knowledge, the producing reservoir can be defined and developed with the least amount of investment and optimal recovery of the resource.

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Horizontal Wells in the Devonian Shale

CONTRACT INFORMATION

Contract Number DE-AC21-89MC25115

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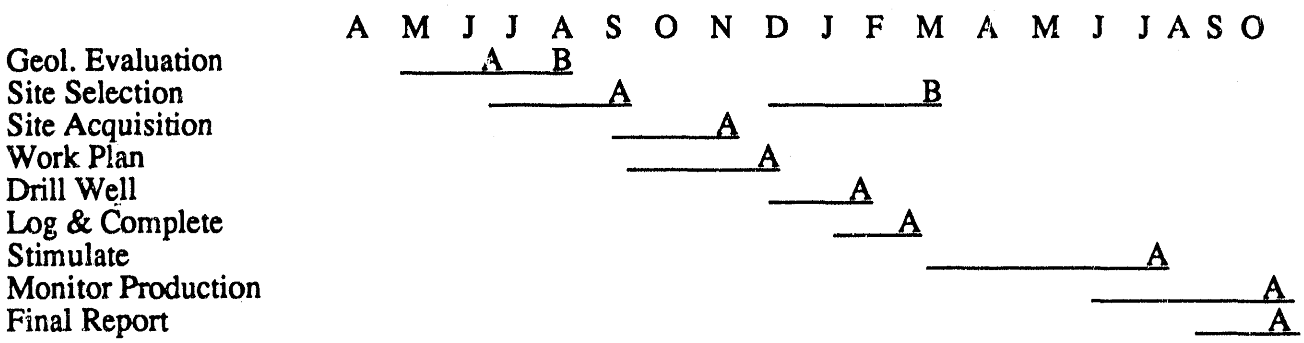
Period of Performance April 25, 1989 to December 24, 1990

Schedule and Milestones

FY 89-90 Program Schedule



A - Cabot Well
B - CNGD Well

OBJECTIVES

The objective of this project is to obtain data that wili determine the economics of drilling a horizontal well completing it with multiple hydraulic fracture stimulations, and comparing the resulting gas productivity with that from conventional vertically drilled and stimulated wells in the test area. A further objective was to transfer the technology to industry through cost-sharing cooperative projects.

BACKGROUND INFORMATION

BDM Engineering Services Company (BDMESC) developed cost-sharing agreements with two Appalachian basin operators, Cabot Oil and Gas Corporation (Cabot) and Consolidated Natural Gas Development Company (CNGD) to address the problems of finding a location that was in a proved productive area and would have sufficient reservoir pressure to provide a successful test of the beneficial effects of horizontal wells both unstimulated and stimulated.

PROJECT DESCRIPTION

Geologic Evaluation

BDMESC geologists developed a working model of the tectonic evolution of the Appalachian Basin area to identify the key structural elements that would impact gas production form the Devonian Shales. Three key structural trends which are elements inherited from continental collision (Grenvillia with North America), rift basin development (Pre-Cambrian Rome Trough), and planetoid rotational shear trends were identified. The Rome Trough was selected as the area within which fracturing from older and younger tectonic episodes might effect reservoir properties and thus, production rates. These trends are indicated in the drainage map presented on Figure 1.

BDMESC reviewed, with Cabot, areas where Cabot had extensive acreage holdings which would comply with the primary area selection criteria of being currently productive and have reservoir pressure of at least 300 psi. The area which met this criteria consisted of 40,000 acres located mostly within Putnam County, West Virginia. Three specific areas of approximately 1,000 acres each were selected for further study based on the projection of having the potential of producing at least 300 million cubic feet of gas from vertical wells drilled in the area Figure 2). DOE selected two of the three study areas for more detailed studies. The area eliminated appeared to have some potential for producing minor amounts of water from the shales. The water was believed related to water in fractures from deeper down-faulted areas of the Rome Trough.

Site Selection

Data from most of the vertical wells drilled in the two areas were compiled into a simple data base. The database included stratigraphic, structural, and production data. Structure maps on top of the Berea, Lower Huron Shale, and the Onondaga limestone were prepared along with isopach maps of these intervals. Major structural trends were identified in local areas through this mapping. Mapping of the structure on the base of the lower Huron Shale in the area (Schafer, 1979) revealed the combined effects of ancient Grenvillian continental collision fracture trends (N-S) with later Pre-Cambrian age rift faulting to create the Rome Trough and later reactivation and reversal of some blocks to produce closely spaced anticlines and synclines along with thicks and thins in sediments. Developing a time sequenced geologic model of the orientation of major structural elements provided insights into the location of areas of tectonically enhanced permeability.

Maps relating to reservoir properties and gas production were prepared to assist in the site selection process. These maps prepared included the following: Initial Open Flow Production, Initial Reservoir Pressure, One Year Cumulative Production, Three Year Cumulative Production, and Total Cumulative Gas Production, Stress Ratio, Reservoir Quality Factor, and Projected Ultimate Economic Gas Recovery.

These maps all seemed to define areas of higher production paralleling Rome Trough, Grenvillian and CSD, fracture orientations. Detailed mapping of local structures indicated a mixture of large and small (200-300 acres) block-like highs which are associated with wells having higher cumulative production . Such a site was located in area 2 within a fairway that projects more than 300 million scf of gas per well of cumulative production from the Devonian Shale (see Figure 3).

Work Plan

After approval of the drill site by DOE and Cabot Oil and Gas Company, BDMESC prepared a plan of drilling operations directed to the specific site. A well prognosis was prepared projecting depths at which various formations were expected. These data were used to design the casing program. The well was planned to turn from vertical to horizontal at a constant rate of turn of 8 degrees per hundred feet. The well was planned to be as economical as possible so an 8 5/8" hole protection casing string was eliminated from the plan. The well was designed to be horizontal in the lower Huron Shale Zone, which has a high degree of natural fracturing as indicated by the frequency of shows reported by mud logs and other types of logs in offsetting wells.

Drilling Operations

Drilling operations were initiated on November 30, 1989 and completed on December 29, 1989. The straight hole section down to the kick off point was drilled in thirteen days. Drilling of this section was delayed four days because of lost circulation problems. Seven days of directional drilling was required to turn the well to 90 degrees, another six days were required to complete the horizontal drilling. Figure 4 presents planned versus actual trajectory of the Hardy HW #1 well. Logging and casing operations were completed on January 2, 1990. Fifty-nine shows of gas were encountered during drilling operations, the largest calculated to be 178 mcfpd at a measured depth of 5616 feet. When drilling operations were completed at a measured depth of 6404 feet, open flow production was gauged at 18 mcfpd. The rapid depletion of all of the fractures encountered by the wellbore indicated that stimulation by hydraulic fracturing was required.

Logging and Completion Operations

Gamma ray, compensated density, temperature, differential temperature, and caliper logs of the wellbore were obtained in the shallow hole above the kick off point and in the inclined and horizontal sections of the well below the kick off point. An attempt was made to obtain a video camera survey of the wellbore, but only a short section of the inclined wellbore was logged before failure of the video logging system.

Well logs were used to select points for setting the external casing packers and to divide the well into four productive partitions for separate stimulation. Casing (4.5", J-55, 10.5#/ft) was installed to 6150 feet depth containing four TAM International* inflatable casing packers and four ported collars to be used for formation access. Final wellbore configuration is presented in Figure 5.

Stimulation Operations

Four hydraulic fracture stimulations were attempted on the well during the period from February 14 to April 1, 1990. Three of the stimulations were successful (those in zones 1, 3, and 4) while two stimulation attempts in the 742' long zone 2 failed. The exact reason for failure to stimulate zone 2 may never be known but we postulate increased stresses in the zone and too much wellbore being addressed by the stimulating fluid as the likely causes for failure. Zone 1 was stimulated with 76,000 gallons of foam and 140,000 lbs of 20/40 mesh sand. Zone 2 accepted 23,000 gallons of foam and 8,000 lbs of sand before the pressure limit was exceeded halting the job. Zones 3 and 4 were fraced together with 1.8 mmcf of nitrogen.

Final open flow gas production from the well after all stimulation operations were completed was 550 mcfpd. Reservoir pressure measured during a 10-day pressure build-up test was 680 psi with absolute pressure projected to be 767 psi using Horner's technique. Reservoir testing and analysis revealed a six-fold increase in production capacity.

Well Test and Analysis and Production Monitoring

After stimulation operations and the initial pressure build-up test were completed; the well was opened up for a production test on May 16, 1990. The results are presented in Figure 6. The initial flow rate was intended to be 100 mcfpd, but freeze-ups during the first week allowed only about 60 mcfpd. After a methanol injector was installed, the rate was maintained at approximately 100 mcfpd using a choke. After about 50 days the well was taken off of choke for a short term test and production increased to 150 mcfpd and some water started to be produced. The well is currently averaging between 90 and 95 mcfpd at a average bottomhole pressure of approximately 125 psi..

For the first 150 days, the well averaged in excess of 100 mcfpd while the producing bottomhole pressure declined from approximately 625 psi to 125 psi. Based on early production, BDMESC projects the well will produce 475 million scf of gas over the next 30 years (See Figure 7). To be a completely economically successful well, it would need to produce more than twice its current 90 mcfpd rate and produce 400 million scf of gas during the next five years. Of course, an increase in the price of gas would change the economics considerably. The Hardy #1 well does produce gas at a rate at least 2.5 times that of the average vertical well drilled in the area.

RESULTS

The Cabot Hardy HW #1 well was successfully sited and drilled according to the drilling plan. More than 59 gas shows indicate that fractured terrain was drilled. Rapid depletion of fractures indicated the need for stimulation of the well.

Stimulation operations on the well were not as successful as drilling operations. Four stimulations were attempted. Only one stimulation was considered conducted as planned while the remaining three were not considered completely successful. After a gross failure to stimulate the 742 food long second zone, zones 3 and 4 were stimulated together to reduce clean-up costs.

When the wells were open flowed to clean-up and test after stimulation, the initial open flow rate (550 mcf) was less than hoped for (750 mcfpd) and fell off quite rapidly.

Stabilized flow rates were considerably less than that needed to pay out for the well in a five year period which was the targeted results. The well is projected to produce 200 million scf of gas in five years and needed to produce 400 million scf of gas in the same period. These results could well be related to the failure to adequately stimulate the well. Additional studies on stress data before stimulation would have been helpful.

CURRENT PROJECT STATUS

The project is a two well project. The first well has been drilled, stimulated and is currently producing gas. The second well will be drilled during November 1990 in Calhoun County, West Virginia. Stimulation should be completed and the well placed in line by April 1991. Final report for the project will be completed by June 1991.

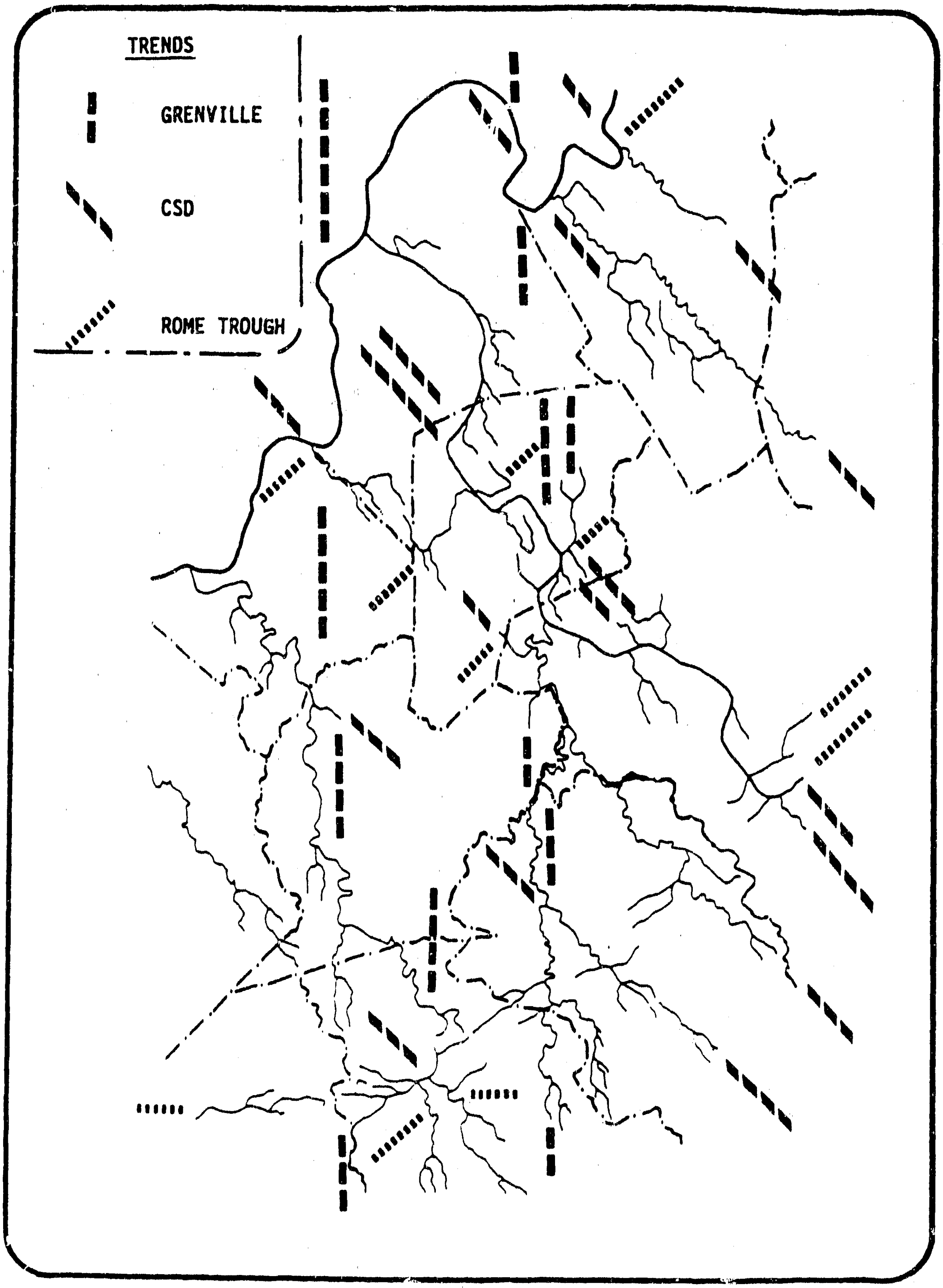


Figure 1 - Structural Trends, Western West Virginia

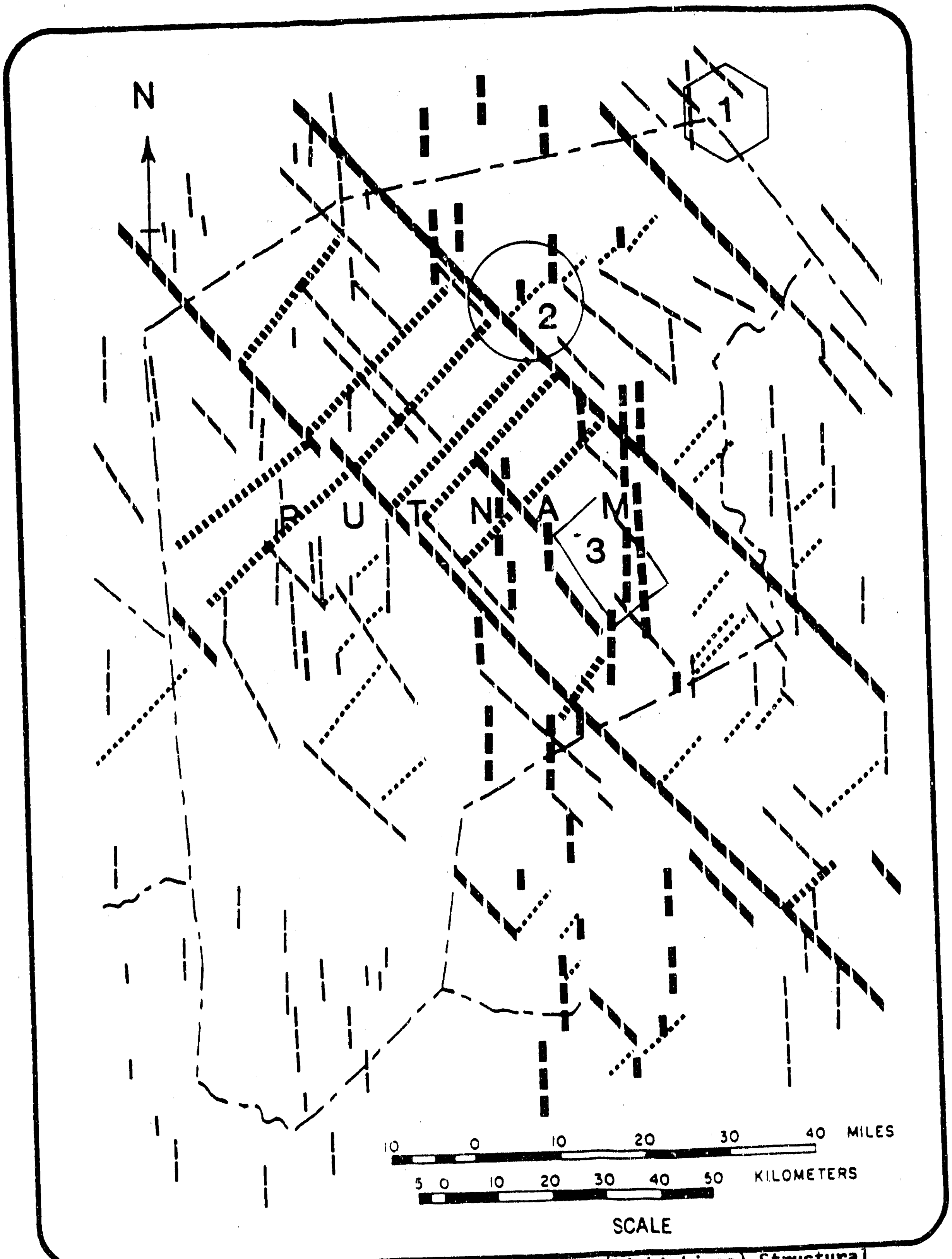


Figure 2 - Cross-State (Heavy Lines) and Local (Light Lines) Structural Trends in Putnam County

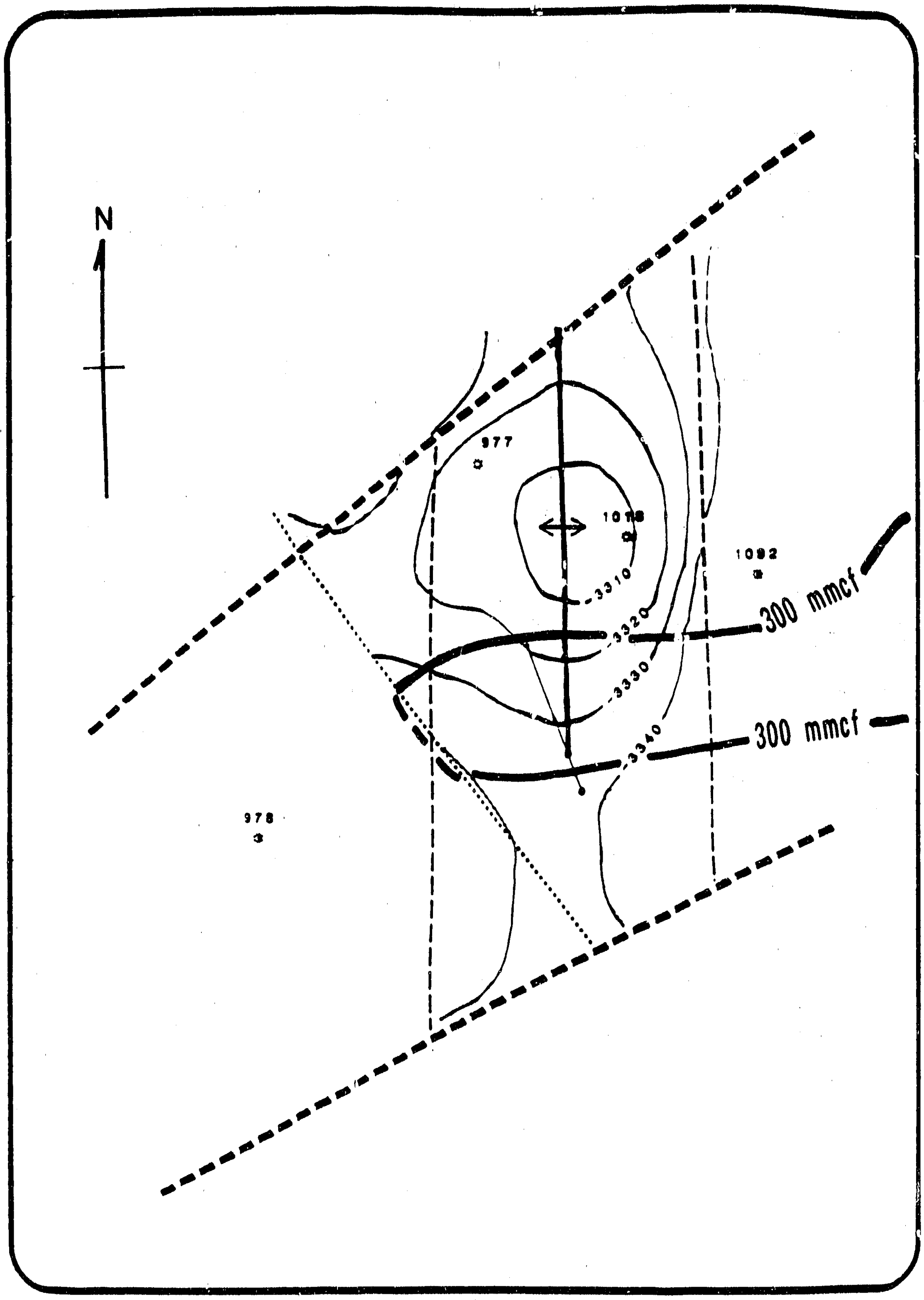


Figure 3 - Relationship of the Planned Wellbore Trajectory to Structure on the Base of the Huron Shale

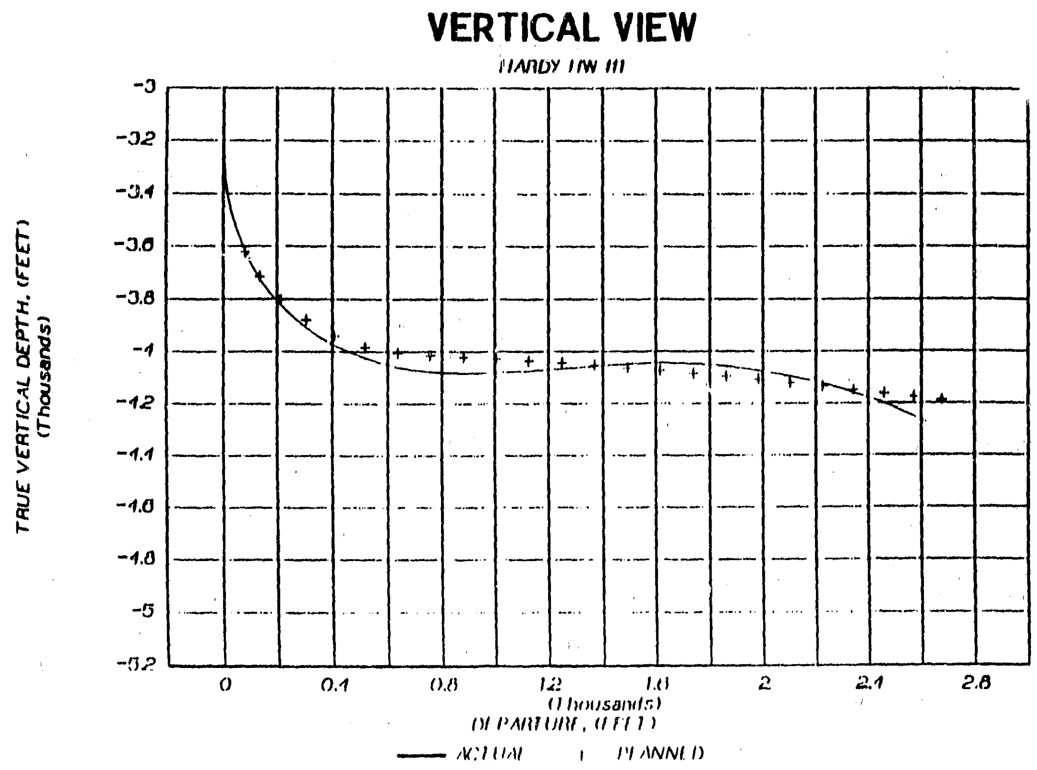


Figure 4

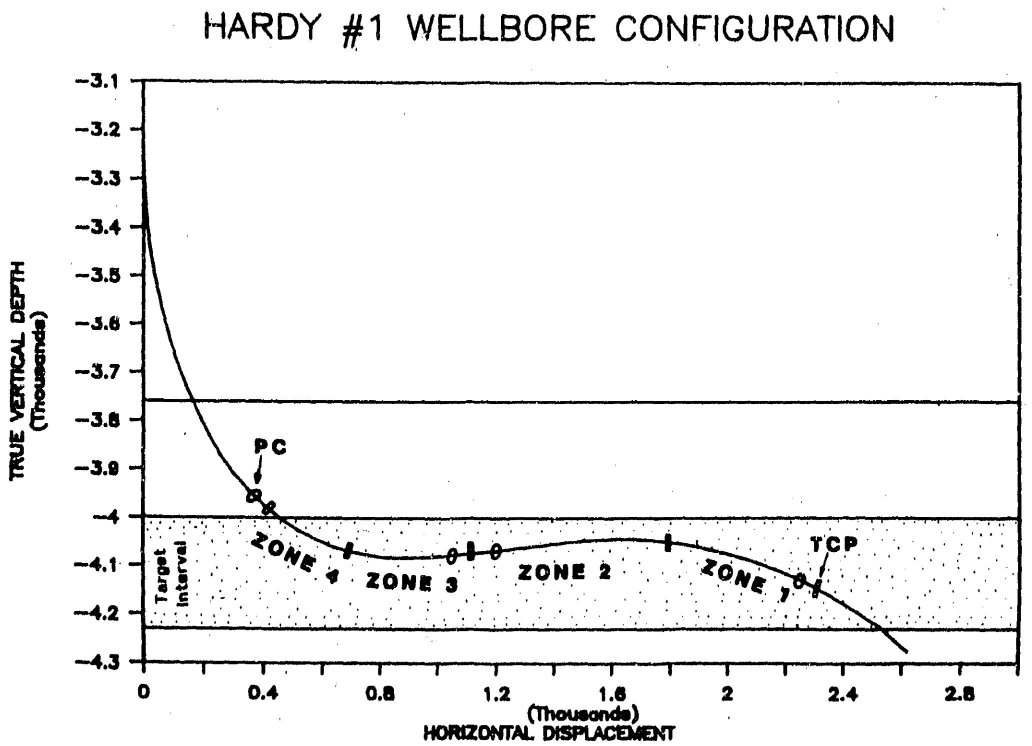
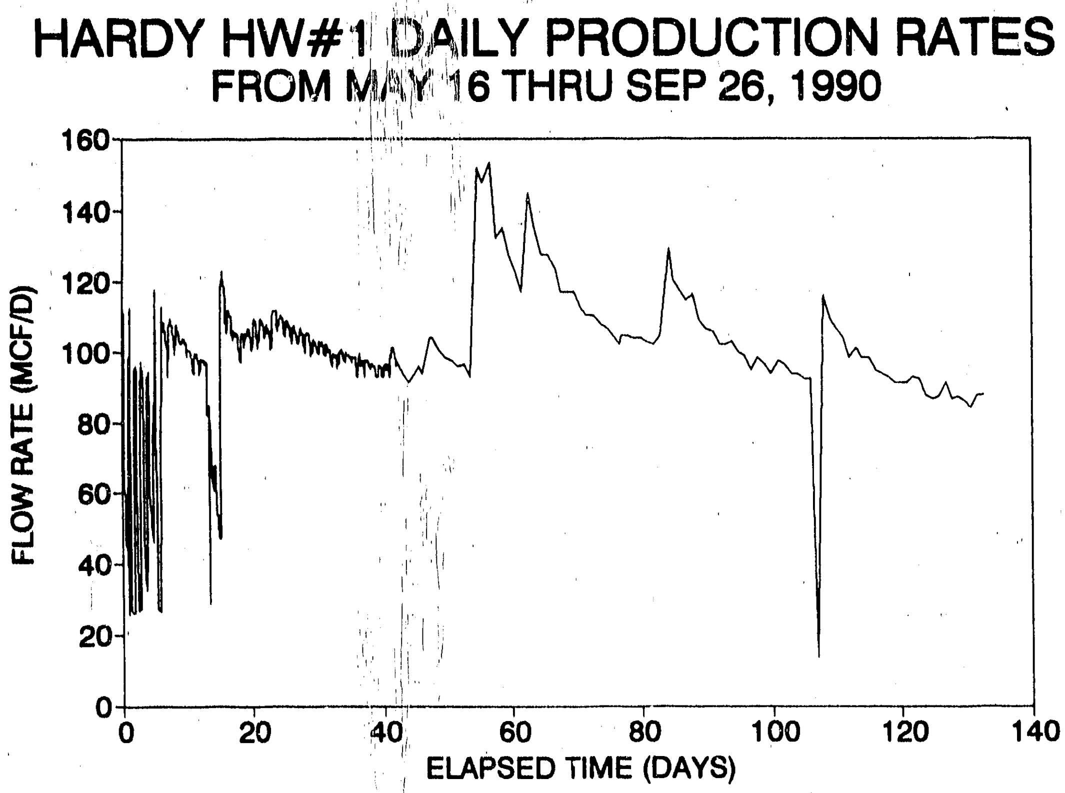


Figure 5


HARDY HW#1 DAILY PRODUCTION RATES
FROM MAY 16 THRU SEP 26, 1990
FLOW RATE (MCF/D)
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
ELAPSED TIME (DAYS)

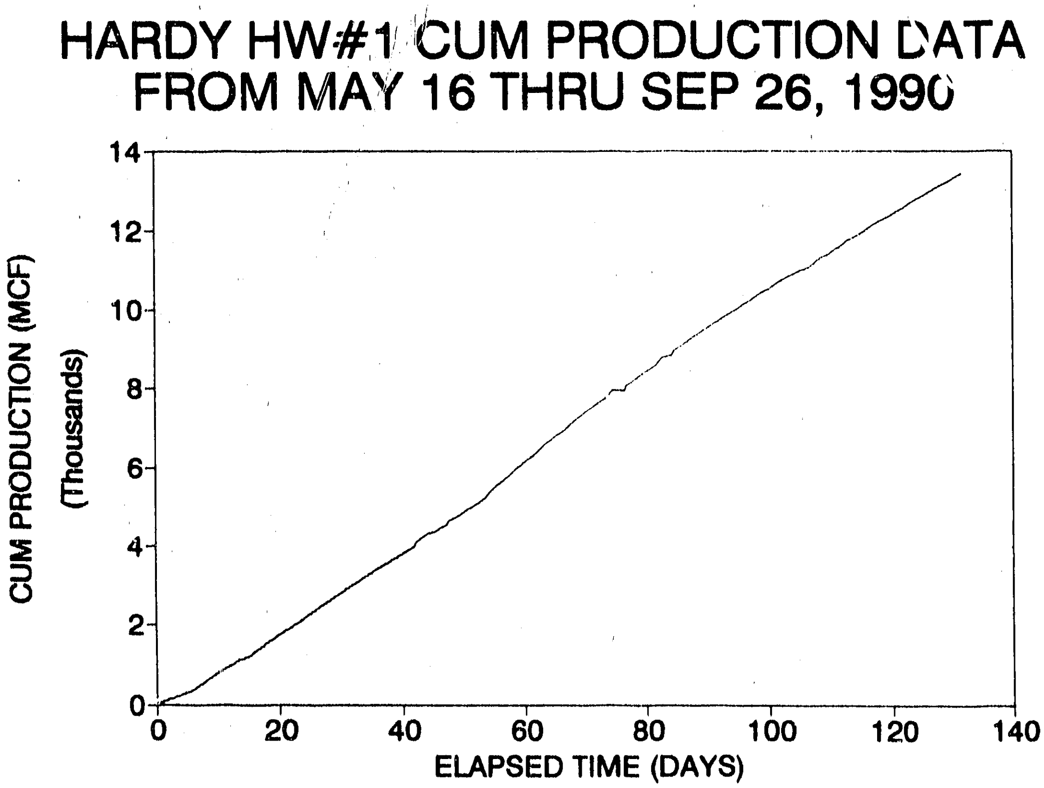
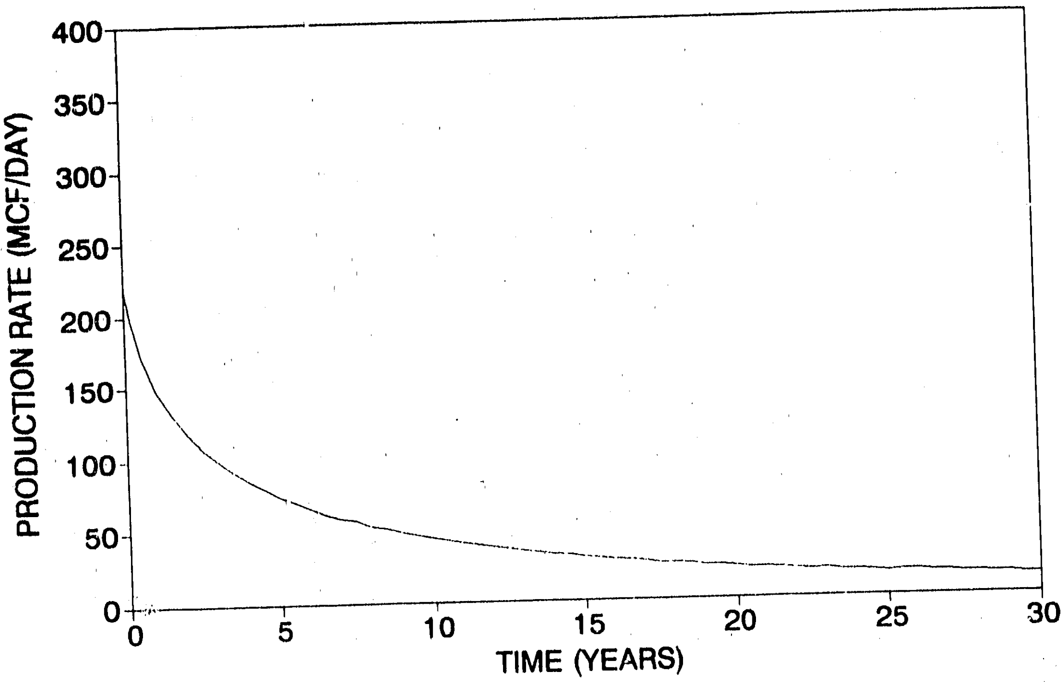

HARDY HW#1 CUM PRODUCTION DATA
FROM MAY 16 THRU SEP 26, 1990
CUM PRODUCTION (MCF)
(Thousands)
14
12
10
8
6
4
2
0
0
20
40
60
80
100
120
140
ELAPSED TIME (DAYS)

Figure 6

PROD RATE PROJECTION FOR HARDY#1 USING GAS RESERVOIR SIMULATION (G3DFR)



PRODUCTION PROJECTION HARDY #1 USING GAS RESERVOIR SIMULATION (G3DFR)

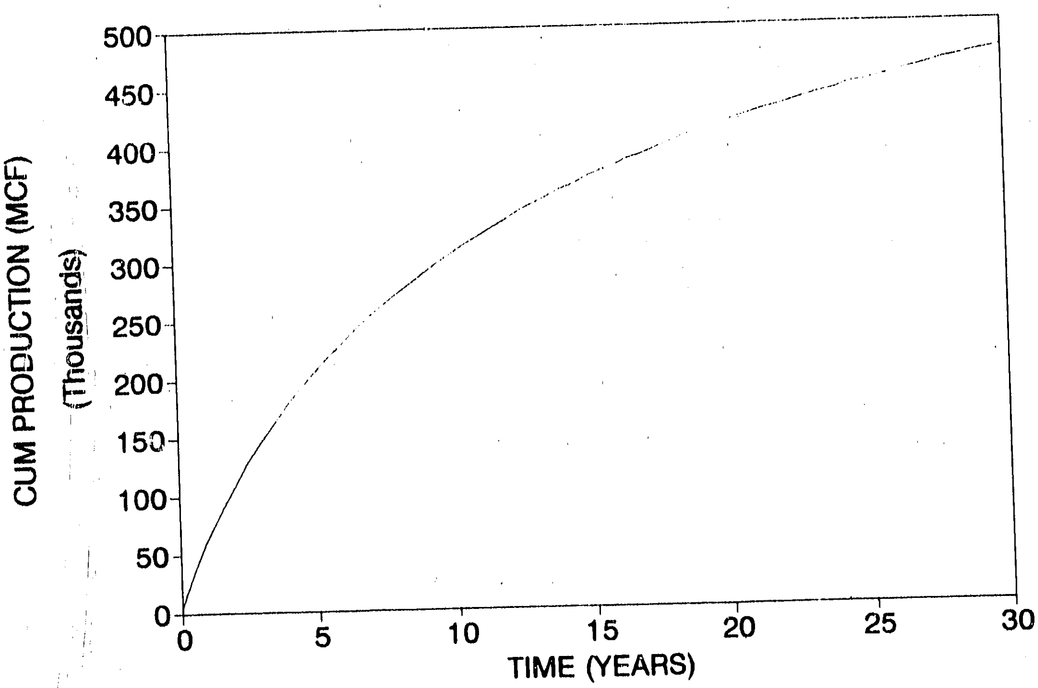


Figure 7

Drilling and Completion of a Horizontal Devonian Shale Well: Martin County, Kentucky

CONTRACT INFORMATION

Contract Number DE-AC21-89MC26343

Contractor Columbia Gas System Service Corporation
1600 Dublin Road
Columbus, Ohio 43215
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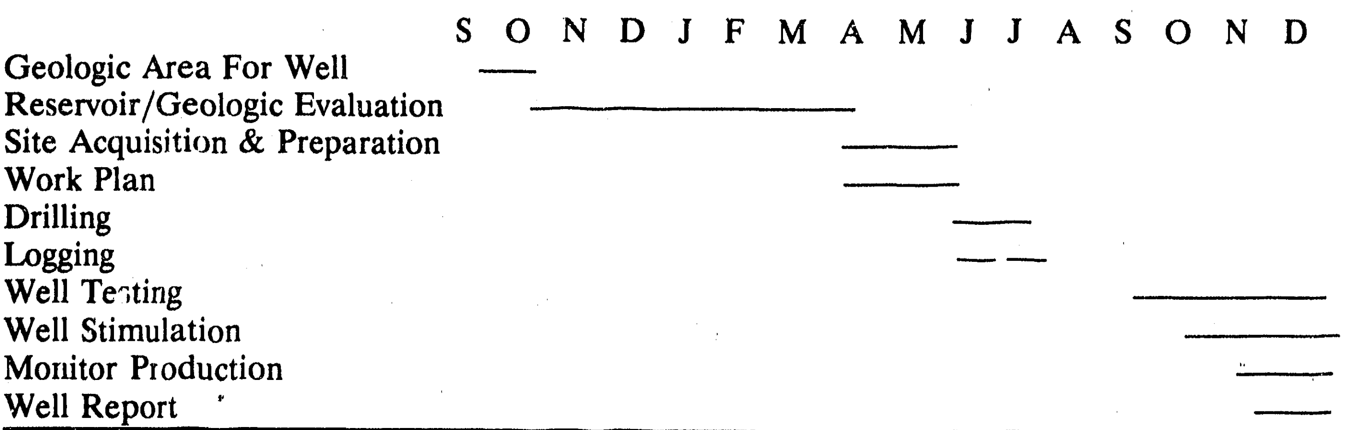
Principal Investigators Gregory Koziar
Mian M. Ahmad (Columbia Natural Resources, Inc.)
Larry L. Friend (Columbia Natural Resources, Inc.)

METC Project Manager Albert B. Yost II

Period of Performance September 29, 1989 to November 28, 1990

Schedule and Milestones

FY 1990 Program Schedule



OBJECTIVES

The overall purpose of this project is to evaluate the technical and economic feasibility of hydraulically fracturing a horizontal well completed in the Devonian shale.

BACKGROUND INFORMATION

Columbia Gas and DOE are participating in cofunded project designed to assess the effectiveness and economic viability of applying horizontal well technology to the Devonian shale. Columbia's well is one of three wells in a DOE program called "Horizontal Wells in the Devonian Shale."

Successful application of horizontal well technology to the Devonian shale requires demonstration that a horizontal well can be economically drilled and that the resulting gas production is economically more attractive than that of a conventionally drilled vertical well.

While a horizontal well may be a technological success, proper assessment of the technology would not be possible if the well were not favorably located. Therefore, to provide the greatest opportunity for realizing the project goals, geographic areas within regions of historic, but undeveloped production, were identified. Regional geology, reservoir quality, proximity to existing production, undeveloped acreage blocks and access to pipelines were major factors driving selection of the areas.

Well 21747, located in the Pigeonroost Prospect in southeast Martin County, Kentucky, was selected as the site for the horizontal well installation.

PROJECT DESCRIPTION

This project consists of nine base and five optional tasks. The base activities were devised to select the most favorable site for the horizontal well and to design and implement drilling, logging, completion and stimulation efforts. Well testing is the only optional task that was executed.

The Program Schedule identifies the individual project tasks. Geologic Area for the Horizontal Well and Reservoir and Geologic Evaluation tasks were undertaken to identify, evaluate and rank candidate locations, and to select a site suitable for the horizontal well.

Once the desired location was identified, site preparation activities commenced. A work plan was devised as a guide for drilling, logging and completion efforts. This was followed by implementation of that plan.

Upon completion of the Well Stimulation and Well Testing tasks, and connection of the well to the gathering line, production will be monitored for five years. A technical assessment of the impact of horizontal well drilling and stimulation on productivity will be made by comparing resulting production between well 21747 and offset vertical wells. Economics will ultimately determine the viability of horizontal well applications to the Devonian shale.

Site Selection

While the site selection process was a critical element of this project, it is only briefly discussed here. Details of the site selection process are located in reference 1.

The Pigeonroost Prospect of Martin County, Kentucky is located near three basement related structural features: the Rome Trough, the Warfield Fault and Anticline, and the Pike County Uplift (Figure 1). As a result this area is expected to be highly fractured.

Within the proximity of available well locations however, little can be discerned in the way of structural or stratigraphic features supporting one location in lieu of another. As a result, the site was chosen primarily on the basis of a favorable production fairways and the availability of a suitable drilling location. Figure 2 shows five year cumulative production values ranging from 100 to 200 MMcf for vertical wells in the area.

Drilling shows, temperature anomalies and production log data from offset wells established a 280 feet interval, consisting of the bottom 100 feet of the Middle Huron and the entire Lower Huron (180 feet), as the primary target window.

Analysis of the azimuths of induced and natural fractures from oriented core, cumulative production trends, and surface lineaments established a desired wellbore heading of N12°W. This direction effectively allowed the well to traverse the production fairway favorably, minimized the anticipated hydraulic fracturing breakdown and treating pressures, and augmented the number of possible intersections between the wellbore and natural fractures.

Drilling

Drilling began June 1, 1990 and ended July 7, 1990. The well reached a measured depth (MD) of 6,263 feet, 3,754 feet true vertical depth (TVD), with a final inclination of 79° and an azimuth of N10°W. A horizontal displacement of 2,872 feet was achieved.

A rig capable of handling maximum hookloads of 260,000 pounds with a rotary table torque of 12,000 ft-lbs was used. Conventional rotary drilling techniques were used for the vertical, tangent and lateral portions of the hole. Downhole motors were used to drill the angle build section.

Both air and foam were used as the circulating medium. Flowing salt water encountered in the Salt Sand necessitated drilling on salt water through the intermediate casing point, the Berea Sandstone.

Drill String. The drill string consisted of approximately 6,500 feet of 4-1/2 ", 16.60 #/ft, grade E drill pipe and 60 feet of 6" nonmagnetic (monel) drill collars. Heavy weight drill pipe was used to provide additional weight during drilling and to help to push tools to bottom. To prevent buckling, bit weight was kept below 25,000 lbs. Figure 3 shows typical drill strings run during angle build and lateral drilling operations.

Bottom Hole Assemblies. Downhole motors were used to drill the angle build section of the hole. Eastman's Mach 1 air motor and Baker's Double Angle Adjustable Bent (DAAB) housing motor were used to drill the angle build section. In total, three motors were run.

Rotating bottomhole assemblies (BHA) were used to drill both the tangent and lateral sections. Figure 4 depicts typical BHA's used during angle build and rotating drilling operations.

Increasing or decreasing the rate of build was achieved by adjusting the bent housing angle(s) when using the downhole motor. Controlling the angle while rotary drilling involved selecting appropriately sized stabilizer(s)/reamer(s) etc. and properly positioning them to achieve the desired results. However, the effect of downhole conditions on a given BHA configuration determined the actual rate of build. In the lateral section, achieving a desired rate of build was essentially a trial and error process.

Directional Control. An electromagnetic measurement while drilling (EMWD) system from Geoservices Inc. was initially run for directional control. The actual survey point was about 61 feet off bottom. Directional information had been obtained over a 35 feet interval, when the EMWD system failed. Both the primary and backup EMWD tools experienced mechanical failure. To take advantage of the benefits of EMWD, additional tool hardening for operation in air drilling environments is required.

The BHA was then reconfigured for a steering tool using a side entry sub. With this configuration, survey readings were obtained 47 feet off bottom.

During lateral drilling operations, single shot surveys were obtained approximately every 200 to 500 feet. The infrequency of surveying during lateral drilling is a result of the time consuming operations of pulling drill pipe, running the survey tool and drill pipe, taking the survey, pulling the survey tool and drill pipe, and rerunning drill pipe.

Upon completion of drilling, a multishot survey was run over the angle build and lateral sections of the well.

Vertical Hole. After setting 20" conductor casing in 24" hole, 17-1/2" hole was drilled to 828 feet. Surface casing, comprised of 13-3/8", 54.5#, K-55, was set at 791.5 feet and cemented. The intermediate hole size of 12-1/4" was drilled into the Berea Sandstone (the kickoff horizon) and the well was logged. 9-5/8", 36#, K-55 casing was run to 2,954 feet and cemented. An 8-3/4" hole was drilled to 3,035 feet MD, the kickoff point.

Angle Build Section. The angle build section was designed to include a tangent section so that corrections in build rate could be easily made if necessary. From the kickoff point to the tangent section the build rate, using a downhole motor, averaged 10.4°/100 feet.

At 3,426 feet TVD (approximately 45°), a 117 feet tangent section was drilled using a rotating bottomhole assembly. (The angle actually increased at a rate of about 1.2°/100 feet.) The downhole motor was rerun with drilling proceeding to 3,860 feet MD (3,622 feet TVD) at 85.6°. The build rate averaged 13.7°/100 feet over this part of the hole.

At this depth a rotating BHA was run to drill the lateral section; however, while reaming to bottom, a second hole was cut below the original. The rotating BHA was removed, the DAAB's was adjusted and rerun to build angle in the new hole. After several attempts to place the build assembly in the new hole, angle was built to 87.9° at 4,153 feet MD (3,680 feet TVD).

Lateral Hole. A rotating BHA designed to maintain a slight drop through the target interval was run. However, angle continued to build to a maximum angle of 96° at 4,700 feet MD (3,649 feet TVD). Several changes in the BHA reversed the angle build tendency and resulted in a gradual drop of 1.0°/100 feet through the target zone. Drilling continued to a depth of 6,263 feet MD (3,754 feet TVD). The well profile is shown in Figure 5.

Heavy weight drill pipe was utilized to assure that adequate weight existed at the drill bit. Weight on bit typically ranged between 10,000 lbs and 20,000 lbs during rotary drilling operations and averaged about 4,000 lbs. while drilling with downhole motors.

The drill string was arranged such that the standard drill pipe was placed in the lateral part of the hole while the heavy weight drill was located in the vertical/angle build sections; standard drill pipe was placed above the heavy weight. This is depicted in Figure 3.

Drilling Problems. At a depth of 4,703 feet MD the drill pipe twisted off. This apparently occurred as the drill string was being picked up to run a directional survey. The fish left in the hole consisted of 74 feet BHA, 1,054 feet drill pipe, and 30 feet heavy weight drill pipe. The fish was recovered on the first attempt.

Logging Program

A mud logger was on location during all directional drilling operations. Thirty-five drilling gas shows were noted. Because of the magnitude of gas flow, over 1 MMscfd, smaller gas shows may have gone undetected. Figure 6 contains a plot of the gas shows as a function of measured depth. Completion zones, also shown, are discussed in the following section.

Geophysical logs were run in both the vertical and deviated portions of the well. Free-fall logs included gamma-ray, compensated density, sidewall neutron, temperature and dual induction. A television camera was also run, but severe downhole dusting made it impossible to view the borehole walls for fractures.

Using tool-pusher logging techniques the maximum logging depth reached was 6,088 feet, 175 feet short of the drillers total depth of 6,263 feet. Tool-pusher logs included gamma-ray, lithodensity, sidewall neutron, temperature, and phasor induction. Because of the dusting problems associated with the free-fall television camera logging attempt, the camera was not run in the lateral section.

Several major points of gas entry (cooling anomalies) were noted on the temperature log which correspond to significant mud log gas shows. The gamma ray log indicates that the lateral borehole oscillates across the Middle/Lower Huron boundary or interface. Between 3,772 feet MD (3,603 feet TVD) and 5,790 feet MD (3,690 feet TVD) the well crosses this interface several times.

Completion Program

Mud and geophysical log information were used to establish discrete completion zones. Used in conjunction with the caliper log, placement positions were determined for downhole hardware.

Figure 7 shows the mechanical configuration of the 5-1/2" production string and identifies six completion zones. The end of the well consists of an openhole section preceded by a section of slotted liner. Above this are a series of five CTC Payzone™ Packers and Halliburton FO Completion Tools. Zonal isolation was accomplished by inflating each CTC packer (the element is 10 feet long) and also by cementing. Water was used to inflate the packers.

The original completion plan called for cementing of Zone 6, the interval above the top CTC packer. However, failure of the packer to inflate (the element was apparently ruptured while running the string into the hole) necessitated a change. Cement was pumped through the FO tools in both Zones 5 and 6. All other CTC packers were successfully inflated.

Completion Problems. In preparation for cementing Zones 5 and 6, the injection port of the top CTC was sealed with cement. Upon drilling out the cement in the casing, a casing leak was detected. A subsequent camera run determined that the casing had parted (backed-off); 3,388 feet of casing was pulled. The casing was rerun with a casing patch and successfully reconnected to the 5-1/2" downhole.

Well Testing

Pre-stimulation drawdown and buildup tests were conducted on Zone 1, the open hole/slotted liner section. The flow test was conducted through a critical flow prover using a 3/16" orifice. The reservoir pressure was 350 psia at the beginning of the test. The final stabilized flow rate of 200 Mscfd with a flowing bottomhole pressure of 288 psia was recorded at 168 hours. The calculated absolute open flow from this single point test was 605 Mscfd.

The buildup test was conducted using a downhole pressure gauge set at 3,580 feet MD (3,505 feet TVD). A final pressure of 348.4 psia was recorded at 423 hours.

The tests were analyzed using conventional analytical techniques for a vertical well in a fractured reservoir. (These test data will be reanalyzed using techniques developed for horizontal borehole geometries). Analysis shows a large negative skin factor of about -4.6 and an effective permeability of about 0.08 md for both tests. Based on the test results stimulation was not recommended for Zone 1.

A retrievable bridge plug with a pressure bomb attached was run to isolate Zones 1 and 2. The purpose of running the pressure bomb is to determine whether communication exists between zones through the reservoir (assuming that both the external casing packers and the retrievable bridge plug do not leak). The pressure bomb will remain in place until testing and stimulation of Zone 2 are complete.

A short term test was conducted on Zone 2. An open flow measurement of 103 Mscfd was recorded at the end of 14 hours. The well was shut-in. Surface pressure built to approximately 305 psia in 90 hours. Based on the low flow measurement, a long term drawdown/buildup test for Zone 2 was deemed unfeasible and stimulation was recommended.

Zone 2 is currently undergoing post- stimulation testing. A stabilized reservoir pressure of 320 psig (surface recording) was obtained after shut-in period of 120 hours.

Stimulation

Nitrogen has been selected as the preferred hydraulic fracturing medium for stimulation. Five separate treatments within the Middle and Lower Huron members are anticipated. Treatment sizes ranging from 1.5 MMscf to 2.0 MMscf nitrogen with high injection rates of 100,000 scfm are planned. Pre-stimulation testing will determine the actual need for treatment.

Stimulation Rationale. The preference for nitrogen fracturing in this locale is rooted in both the nature of the reservoir and current stimulation practices. First, the reservoir is highly fractured as a result of three basement related features. Because of this, Columbia feels that stimulation here provides little more than cleanup of drilling induced formation damage and establishes communication between the wellbore and extensive natural fracture system. This can easily and inexpensively be accomplished with the use of nitrogen.

Second, the low reservoir pressure (150 - 350 psi) and high capillary forces combine to make post-stimulation cleanup of the liquid phase of a treatment a very long process. Foam fracturing typically requires 10 to 20 days to cleanup with a service rig on site.

Third, nitrogen has been used almost exclusively to treat over 40 offset vertical Devonian shale wells. Since all wells will be placed on production at about the same time, the horizontal and vertical wells will be effectively producing under the same set of reservoir conditions (assuming that localized depletion of natural fracture sets is not significant).

Although the effectiveness of straight nitrogen fracturing on long-term productivity is uncertain, a definitive assessment comparing the performance of the horizontal and vertical wells under essentially uniform reservoir and operating conditions is assured.

Treatments Performed. To date, one treatment has been performed. Zone 2 was treated with 1.5 MMscf nitrogen at an average injection rate of about 100,000 scfm. The breakdown pressure was 2,555 psi; treating pressure averaged 2,569 psi. After 72 hours of cleanup, a pitot flow of 580 Mcfd was gauged.

RESULTS

The following is a brief summary of the accomplishments and results achieved to date:

- The well was drilled to a total depth of 6,263 feet MD, 3,867 feet TVD. Total horizontal displacement is 2,872 feet.
- The maximum drift angle achieved was 96°. The angle was dropped over the last 1,200 feet of hole to allow the well to drift across the target interval; the final well inclination is 79°.
- The well consists of six completion zones: an openhole/slotted liner section; three cased, uncemented sections containing sliding sleeve completion tools isolated by external casing packers; and, two cemented zones.
- Drawdown and buildup tests conducted over the open hole/slotted liner section revealed that this interval does not require stimulation. An absolute open flow of 605 Mcfd was calculated from a single point test for this zone. Reservoir pressure is 353 psia.
- Zone 2, isolated by external casing packers, has been stimulated with 1.5 MMscf straight nitrogen injected at a rate of 100,000 scfm. This zone is currently undergoing testing.

FUTURE ACTIVITIES

Remaining work on the project consists of conducting pre- and post-stimulation testing as appropriate. Test results will determine the need for stimulation. If stimulation is necessary, straight nitrogen fracturing will be performed.

Upon completion of all field activities and after the well is tied into a gathering system, production will be monitored for a five years. Production comparisons will be made between that of horizontal and offset vertical Devonian shale wells.

Lastly an economic analysis will be performed to determine the viability of applying horizontal drilling to the recovery of Devonian shale gas.

REFERENCES

Koziar, G., et al. June 1990. *Devonian Shale Horizontal Well Site Selection,* Topical Report. DOE Contract No. DE-AC21-89MC26343.

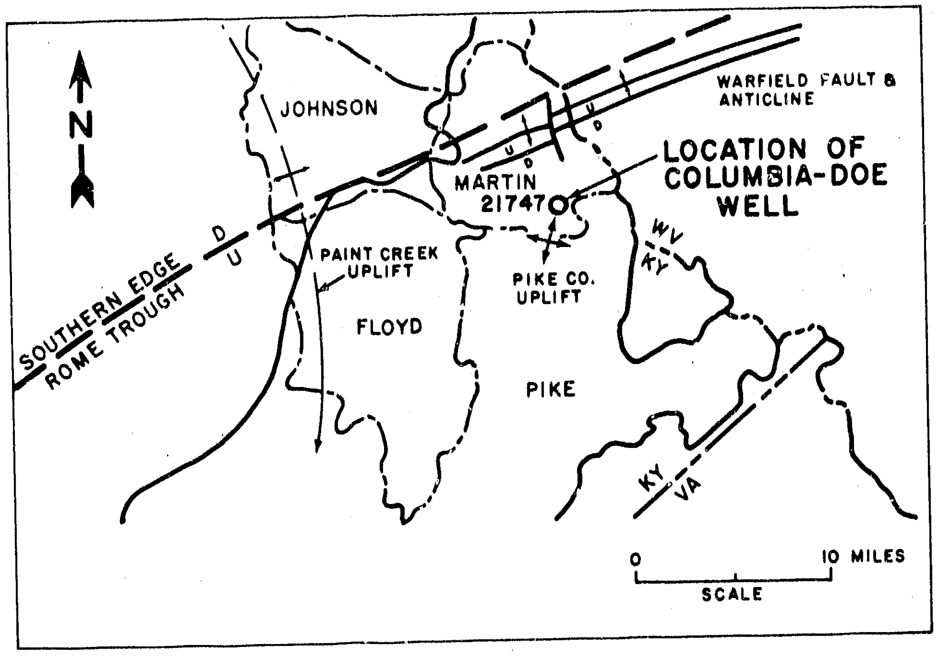


Figure 1. Regional Structure and Well Location

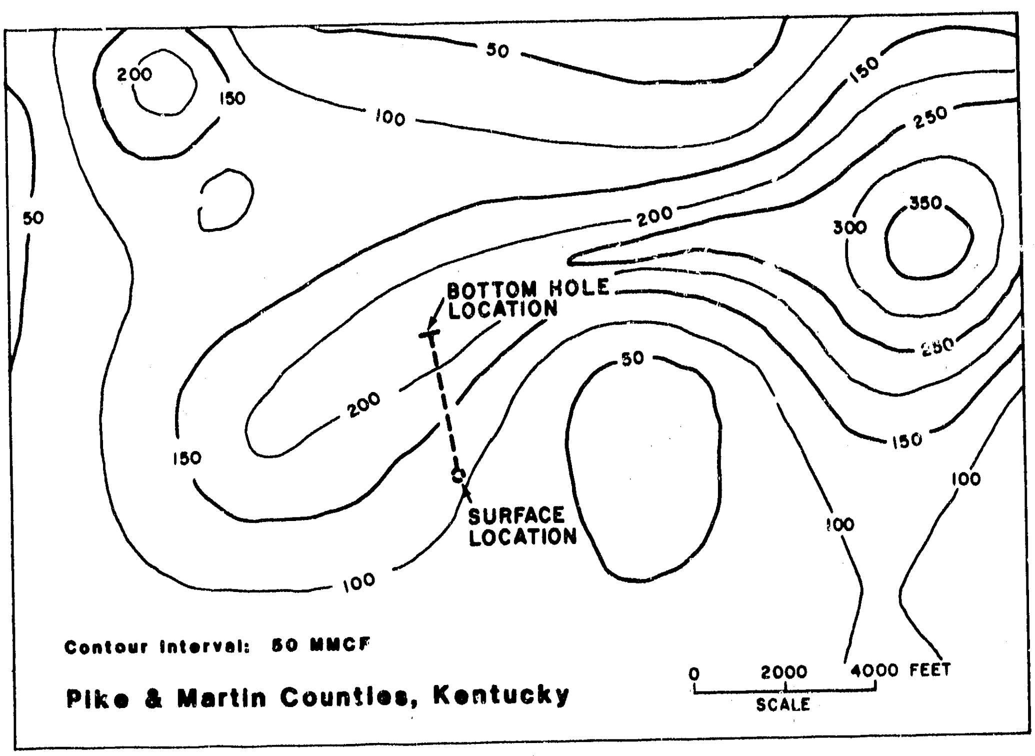
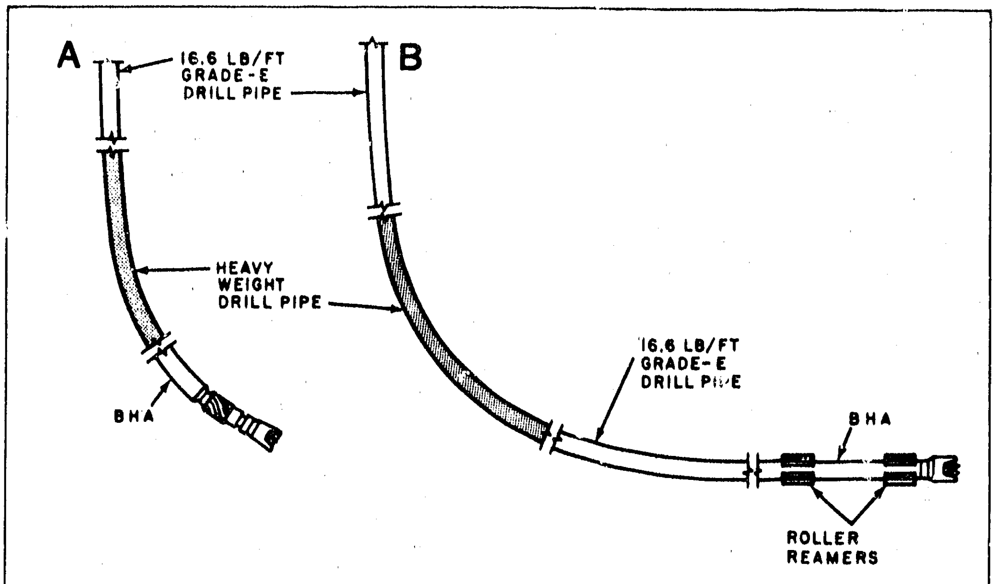
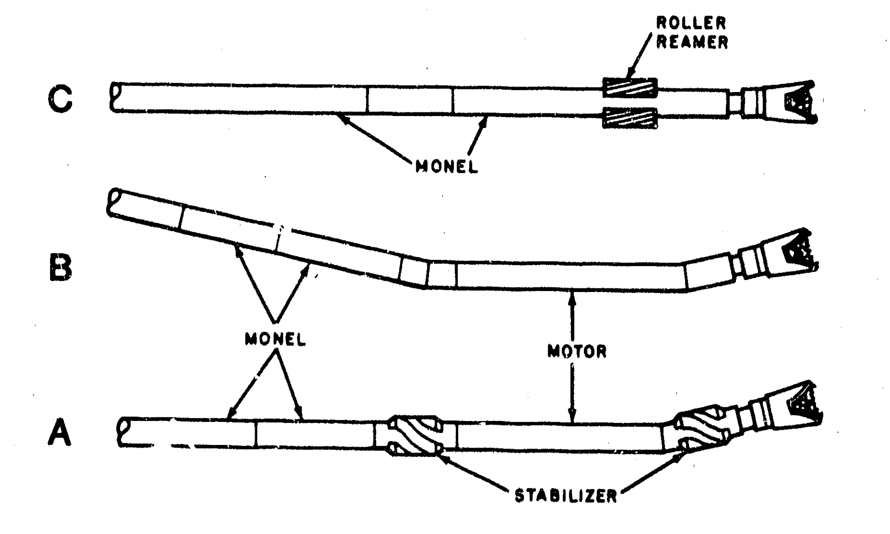


Figure 2. Five Years Cumulative Production



A. Angle build section with downhole motor assembly. **B. Lateral section with rotating assembly.**

Figure 3. Drill String Configurations



Typical BHA's used to drill the angle build section (A & B) and the tangent and lateral sections (C).

Figure 4. Bottom Hole Assemblies

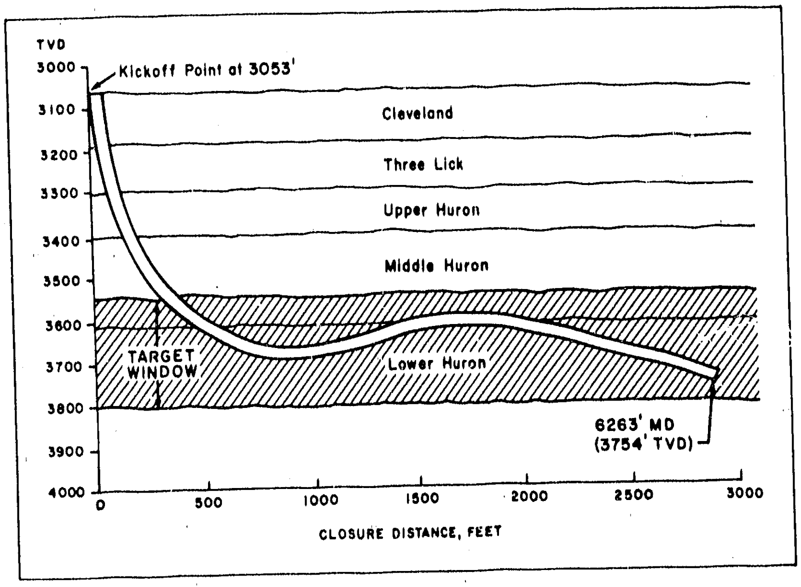


Figure 5. Horizontal Well Profile

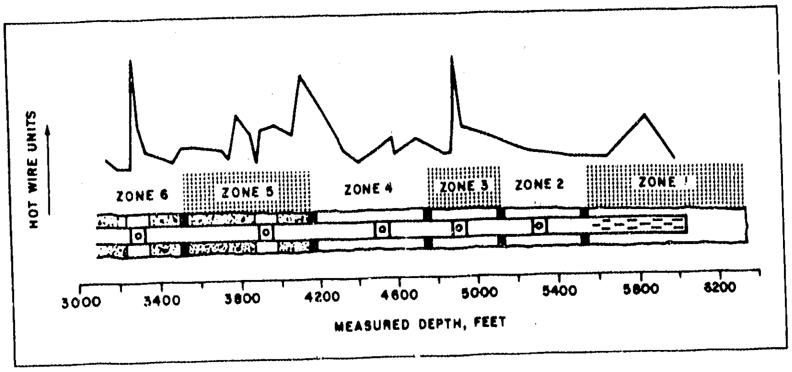


Figure 6. Mud Logger Gas Shows

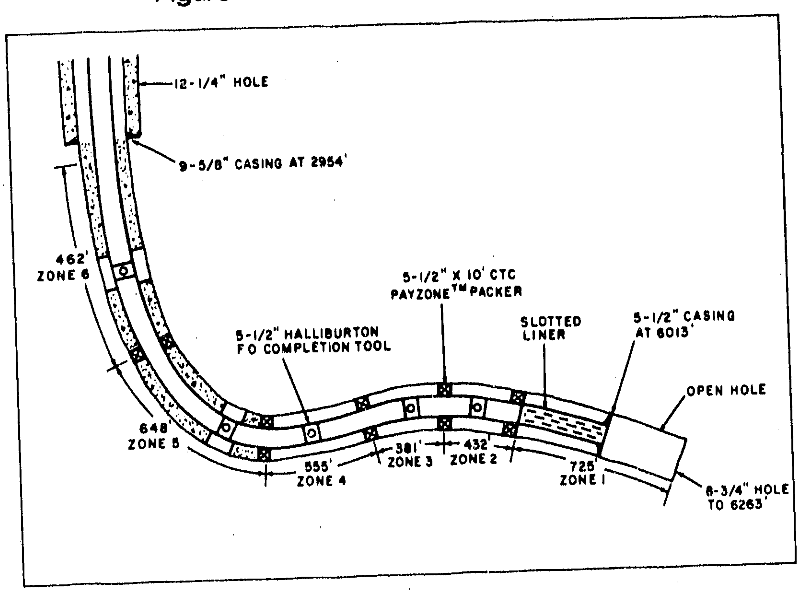


Figure 7. Completion Configuration

PrimeEnergy/DOE/GRI Slant Well: A Directional Drilling Case History

CONTRACT INFORMATION

Contract Number	DE-FC21-88MC25146
Contractor	PrimeEnergy Corporation One Landmark Square Stamford, CT 06891
Contractor Project Manager	Charles E. Drimal
Principle Investigators	Charles E. Drimal Gery Muncey
METC Project Manager	Albert Yost II
Period of Performance	October 30, 1988 to September 30, 1990

ABSTRACT

This paper presents preliminary results of a high-angle Devonian Shale development well in the Alleghany Plateau of west central West Virginia. The well was drilled on the foreland flank of the Chestnut Ridge anticline; a structure closely associated with a fairway of locally significant Devonian Shale gas production. The target of the well was a tabular, southeast-dipping, fractured zone near the top of the Lower Huron member of the Devonian-age Ohio Shale.

The well was conventionally drilled to a kick off point of 2,150 feet. Positive displacement motors were then used to build inclination, at an average of 9° per 100 feet, to an inclination of 67° at a true vertical depth of 2,954 feet. Conventional rotary assemblies were then used to drill the slant section of the well, across a 1,500-foot target section, to a true vertical depth of 3,571 feet. Inclination in the slant section varied from 67 to 72°.

Hydraulic fracturing treatments were performed in four separate stages. Stimulation intervals ranged in length from 6 to 570 feet. Each interval was treated with straight nitrogen in volumes ranging from 1,170,000 to 1,800,000 standard cubic feet after breakdown with 400 to 500 gallons of 7.5% acid. Aggregate open flow from all zones tested at 1,400,000 standard cubic feet per day; approximately a three-fold improvement over the average vertical well in the area.

An economic model is presented which suggests that risks associated with fracture distribution and gas recoverable from individual fractured zones can render a directional drilling program uneconomical, pointing to the importance of well-site selection and well design. Economic success or failure of this project is, as

yet, uncertain. The economic success of directional drilling as a strategy in the Devonian Shale, however, will be revealed only as many more such wells are drilled.

INTRODUCTION

This paper presents preliminary results of the Sterling Boggs 1240 slant well. The Boggs 1240 was drilled under DOE Cooperative agreement No. DE-FC21-88MC25146 as part of an ongoing DOE investigation of directional drilling in the development of marginal gas resources. The United States Department of Energy and PrimeEnergy Corporation (successor to Sterling Drilling and Production Company) developed a cost sharing contract under which the high-angle well would be drilled, logged, tested, and stimulated. Early-on in the project, the Gas Research Institute (GRI) joined as a research participant to conduct supporting research in well sitting, well logging, testing and stimulation, and PrimeEnergy was joined by Columbia Natural Resources, McCormick Resources and the Pennzoil Company as working interest partners.

Objectives of the project were (1) to test the potential for improved recovery efficiency from a directionally drilled well, (2) to perform detailed tests of reservoir properties and completion methods, and (3) to provide technology to industry which may significantly improve the economics of drilling in the Devonian Shale and thereby stimulate development of its resources.

This paper updates information presented in an earlier paper (Muncey 1989a) regarding the background and plans for the slant hole project. Like the earlier paper, this paper is influenced by the investigations of Lowery et al. (1988) and Sweeney (1986) and by communications with many government and private-sector scientists and engineers, particularly in the development of the geological setting.

The paper is divided into five sections. In part I the geologic setting and reservoir character are discussed. Drilling plans and drilling operations are discussed in part II. In part III completions and stimulation results are presented and the economics of directional drilling is discussed in part IV. A summary and conclusions are presented in part V.

I. GEOLOGIC SETTING

The study area lies within the Alleghany Plateau structural province. The study area and surface expressions of local tectonic features are presented in Figure 1. The structural style of the area is dominated by the intersection of an Alleghanian detachment, defined by the north to northwest-striking Burning Springs and Mann Mountain thrust sheets, and a northeast-striking system of relatively low-amplitude folds. The project well targeted a tabular fractured zone within the Devonian Shale; a thick sequence of thinly-bedded, organic-rich shales which were deposited in a foreland basin of the Alleghany

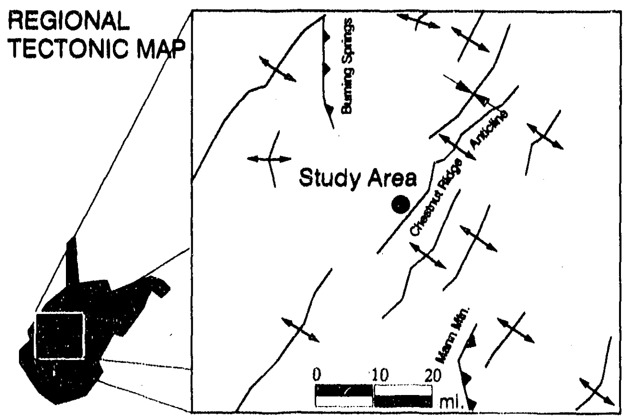


Figure 1. Regional Tectonic Map (modified after Lowery et al. 1988)

orogenic belt. The well was drilled on the foreland flank of the Chestnut Ridge Anticline which lies on the leading edge of the northeast-striking foldbelt.

Local Devonian Shale production is known to be from a fractured reservoir whose presence and quality is fault-controlled. The wellsite is located within a relatively high-production-potential fairway, within which a well-developed fracture system is known to exist. Figure 2 illustrates 12-month cumulative gas production for wells offsetting the Boggs 1240. Contoured values are in millions of cubic feet (MMcf). Dotted lines represent traces of faults, on the top of the Lower Huron, interpreted from repeat sections observed in offset wells (Lowery et al. 1988). Also shown in Figure 2 are the surface location of the Boggs 1240 and the wellbore target azimuth.

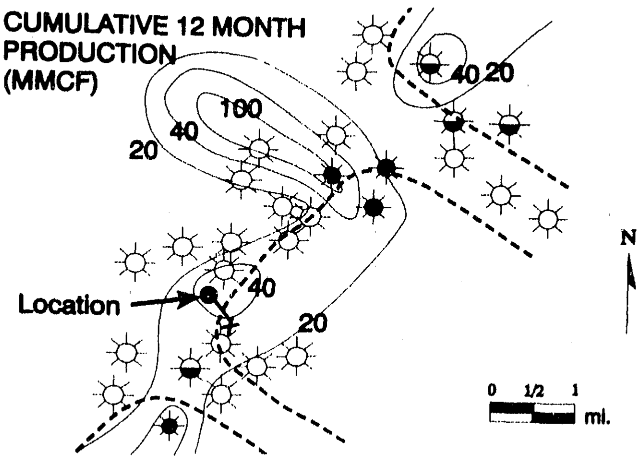


Figure 2. Cumulative 12 Month Production (MMcf) and Fault Traces on the Lower Huron (after Lowery et al. 1988)

First year cumulative production in the area ranges from a high in excess of 100 MMcf to lows of less than 5 MMcf. First year cumulative production is highly variable within the fairway, but a strong systematic correlation with the structural fabric can be observed. It is apparent that the northeast component of the local structural fabric is the dominant influence on the reservoir, and hence that the northeast-trending fractures are of primary importance in the reservoir system. However, it is also apparent that some of the better wells may be associated with a northwest structural trend that has been correlated with Alleghanian shear faulting (Lowery et al. 1988).

II. DRILLING OPERATIONS

Figure 3 presents a schematic of the project-well design, the target zone as envisioned from offset well data, and the actual wellbore as drilled. On the vertical axis is true vertical depth - beginning at 2100 feet subsurface. On the horizontal axis is lateral departure. Stratigraphically, the kick off point (KOP) is just above the top of the Upper Devonian Undivided at about 2,100 feet subsurface. The target zone is located within the lower few hundred feet of the Upper Devonian Undivided and the upper 100 feet of the Lower Huron member. Figure 4 presents the planned and actual well trajectories in plan view. All axes in Figures 3 and 4 are in kilo-feet.

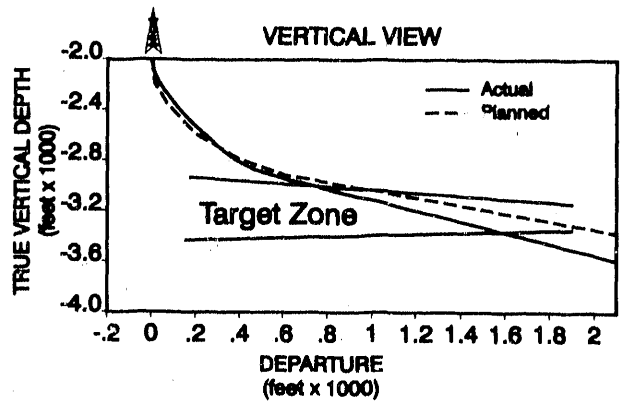


Figure 3. Wellbore - Reservoir Schematic

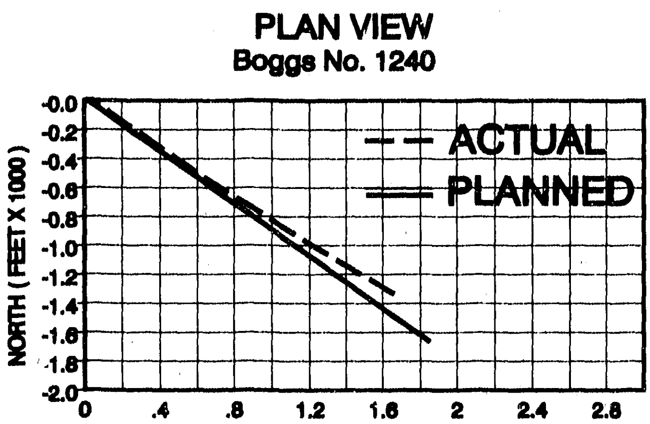


Figure 4. Wellbore Azimuth in Plan View

The well design targets were (1) to be at 68° inclination by 2,950 feet true vertical depth (TVD), plus or minus 50 feet, (2) to attain a lateral departure of 600 feet, plus or minus 50 feet, by 2,950 feet TVD with a target angle-build rate of 8.6° per 100 feet using a double bend motor assembly and steering tool, and (3) to drill across the target zone building angle at about 0.5° per 100 feet using a rotary assembly. The total planned measured depth (MD) was to be 5,160 feet (3,426 feet TVD). Drilling time for the well was expected to be 20 days.

Drilling operations were conducted on site from July 10, 1989, to August 1, 1989. The vertical section of the hole to the KOP took one day longer to drill than anticipated. The angle-build section required 7 days drilling time; approximately what had been anticipated. An additional 2 days were needed to drill the slant section due to an unplanned downhole motor rui as the borehole had begun to walk to the east, getting too close to the adjacent lease and threatening the prospect of too little lateral departure. The motor run did manage to turn the hole back but the wellbore had also lost inclination, causing it to drop out of the target zone earlier that had been planned.

The total wellbore length (total MD) was 4,833 feet; 327 feet shorter than had been planned. Total TVD was 3,571 feet. Days on location totaled 23; as close the plan as could have been expected for a well of this type.

III. COMPLETION AND STIMULATION OPERATIONS

Hachured areas in Figure 5 depict the five intervals within which sustained gas shows were encountered. Based upon prestimulation data, the best of the shows were well below the bottom of the target zone. Offset well data had suggested that the best zone(s) should be expected near the top of the target zone. Moreover, the deeper zones were not even encountered in the offset wells, suggesting the fracture system to be more complex than interpretations of (vertical) well control had predicted.

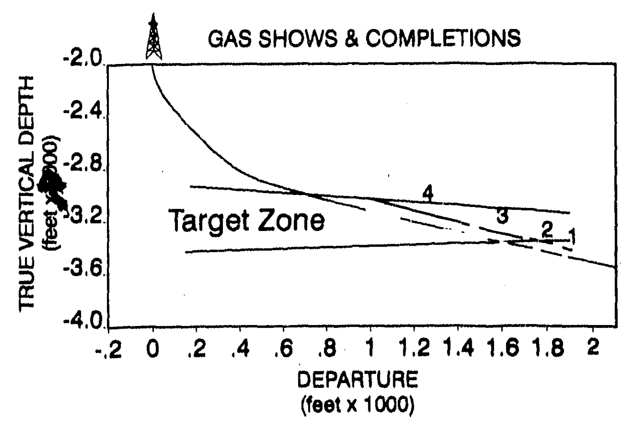


Figure 5. Gas Shows and Completion Stages

Completion stages in Figure 5 are shown schematically by the sub-horizontal bars numbered 1 through 4. Four separate hydraulic fracturing treatments, corresponding to each of the perforated zones were conducted. The stimulation intervals ranged from 6 to 570 feet long. All intervals were treated with straight nitrogen, as were the vertical wells in the field. Nitrogen volumes ranged from 1,170,000 to 1,800,000 standard cubic feet, with injection rates ranging from 70,000 to 80,000 standard cubic feet per minute. Each zone was broken down ahead of the nitrogen with 400 to 500 gallons of 7.5% acid. Individual intervals were isolated with a retrievable bridge plug. Perforating was performed via wireline-conveyed hollow carrier guns using a set of specially designed rollers. Perforated intervals were picked based on the suite of logs which included (1) spectral gamma ray, (2) resistivity, (3) litho-density, (4) sidewall neutron, (5) mud log, (6) temperature, and (7) a borehole camera log. A summary of stimulation treatments and post-stimulation flow rates is presented in Table 1.

Table 1. Summary of Stimulation Treatments

Stage	Interval	Length	Nitrogen Volume	Flow Rate
1	4,618-4,624 ft	6 ft	1,338 Mcf	30-35 Mcf/d
2	4,416-4,563 ft	147 ft	1,546 Mcf	45-54 Mcf/d
3	4,144-4,356 ft	212 ft	1,170 Mcf	40-45 Mcf/d
4	3,466-4,036 ft	570 ft	1,800 Mcf	80 Mcf/d

Production for each stage was measured after nitrogen content had dropped below 10%. Measurements were made through an orifice runaway and back pressure regulator to simulate line pressures of 40 to 45 psig. Flow rates (Table 1) were monitored against line pressure for several weeks in order to establish stabilized flow rates for each zone. Stabilized flow rates for all four zones totaled about 195 Mcf/d. A much shorter duration measurement, meant to approximate open flows as measured at offset wells, totaled 1.4 MMcf/d from the four zones. Both measurements were approximately three times the average equivalent measurement for a vertical well in the area.

IV. ECONOMICS

A histogram of ultimate recoverable reserves for 36 vertical wells offsetting the Boggs 1240 is presented in Figure 6. On the horizontal axis is recoverable reserves in MMcf. On the vertical axis is the number of wells in each of the reserves categories. Reserves were estimated via decline curve analysis of individual wells. Individual production histories were fitted and declined for a total (historical + projected) of 35 years. This differs from the statistically derived type-curve approach presented in the earlier paper (Muncey 1989a), but has led to essentially identical conclusions regarding drilling economics.

An important insight from the revised reserves analysis is that it is now more clear that the distribution of reserves is actually bimodal. A high-reserves population and a low-reserves population are now apparent. Both populations appear to exhibit log-normality. It is also interesting to note that at least two of the three wells which make up the high-reserves population are apparently associated with the northwest structural trend. Assuming log-normality, average reserves for the total population are 68 MMcf per well. Averages for the low-reserves and high-reserves populations are 47 MMcf and 640 MMcf respectively.

Economic modeling (Muncey 1989a) suggests that, at todays prices and cost structure, vertical wells with ultimate recoveries of less than about 150 MMcf are uneconomical to drill, even with the Section-29 tax credit. Selected economic assumptions underlying the minimum economic reserves figure are listed in Table 2. The most important thing to note in Figure 6 is that the success rate implied by the sample population is very low; only on the order of 25%. We can conclude from this that the width and spacing of the fractured zones which characterize the reservoir are such that they make

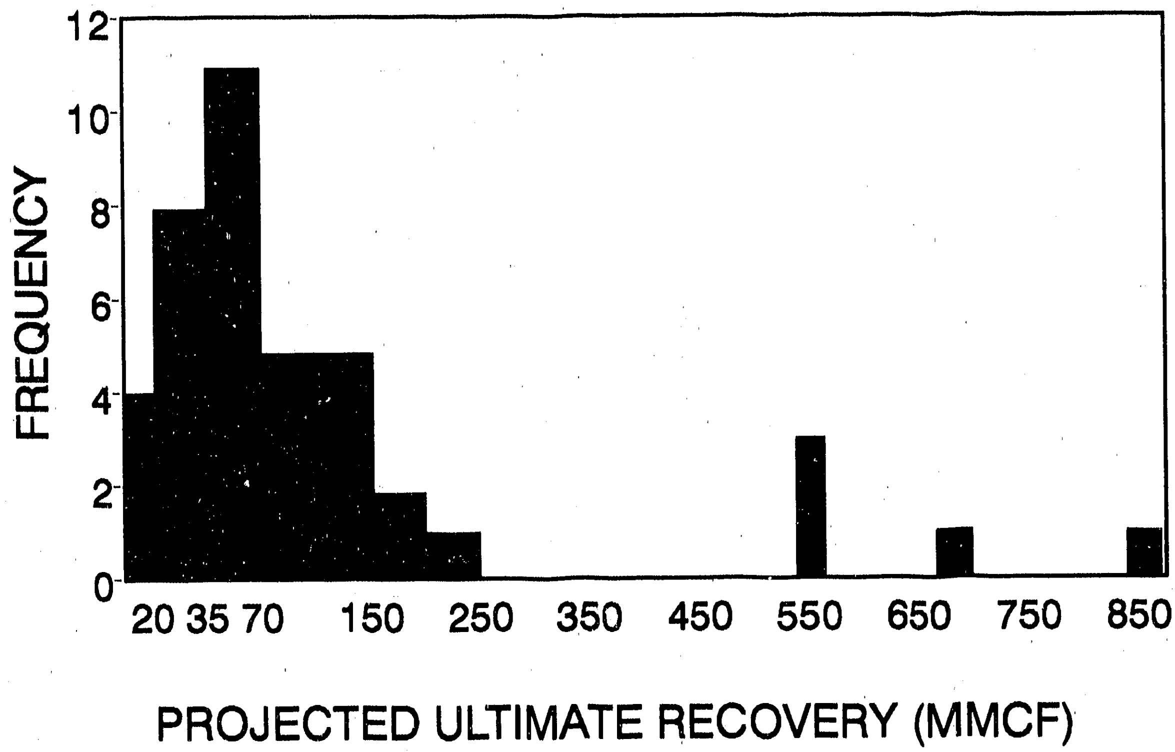


Figure 6. Histogram of Projected Ultimate Recovery

Table 2. Selected Economic Assumptions

Gas Price	\$3.00/Mcf; Escalated @ 5% per year for 5 years, 3% per year thereafter
Operating Expenses	\$280 per month; Escalated @ 3% per year
Net Revenue Interest	87.5%
Taxes	Marginal federal rate = 34% Tax credit per section 29 of U.S. Tax Code
Discount Rate	17%
Well Cost	\$185,000 through completion

excessively risky targets for conventional vertically-drilled wells.

It is logical to assume that we can increase the probability of hitting these fractured zones if we drill across their strike with a high-angle or horizontal well. The question is: is directional drilling an economically feasible solution to poor Devonian Shale economics?

Equation 1 puts the question of economic feasibility into simple mathematical terms. It asks: by what expected factor, E(K), must the expected present value of 150 MMcf, E[PV(150 MMcf)], be increased to make the slant well economical at a non-research cost of approximately \$500,000? In Equation 2 E[PV(150 MMcf)] is reformulated into the product of the probability of finding 150 MMcf of recoverable reserves with a vertical well, Pv, and the present value of those reserves, PV(150 MMcf). For convenience it is assumed that Pv is approximately equivalent to the probability that recoverable reserves from any given fracture system equal 150 MMcf. Substitution of upper and lower limits of Pv into

Equation 2 results in the set of boundary values of E(K) presented in (3).

$$\$500,000 = E(K) * E[PV(150 \text{ MMcf})] \quad (1)$$

$$\$500,000 = E(K) * Pv * PV(150 \text{ MMcf}) \quad (2)$$

$$\begin{array}{l} \text{if } Pv \geq 0.25 \text{ then } E(K) \leq 10.8 \\ \text{if } Pv \leq 1.0 \text{ then } E(K) \geq 2.7 \end{array} \quad (3)$$

For example, we know from our sample of 36 wells that, random vertical drilling should produce a success rate of 25%. Substituting Pv greater than or equal to 0.25 suggests that E(K) is less than or equal to 10.8. Substitution of the upper limit Pv ≤ 1.0 suggests a lower-limit value of 2.7 for E(K). Two conclusions should be clear from this model study. First, the ratio of directional well cost to vertical well cost ($500,000/$185,000 = 2.7) determines only the lower limit of expected reserves required to make directional drilling economically feasible. It can be shown that risk elements of E(K) can be isolated to the statistical character of fracture distribution in the reservoir. Therefore, for a given well design, risks associated with fracture distribution and gas recoverable from individual fracture zones can render a directional drilling program uneconomical. This may happen if, given a particular well design, fracture distribution, and reserves expectations, the well cannot feasibly deliver reserves required to offset expenses. This leads to the second conclusion; that directional drilling, in and of itself, is not a solution to the poor economics of vertical drilling in the Devonian Shale. Rather, it shows that the site selection process and appropriate well design are critical to the economic success of a directional drilling program.

Preliminary production data for the Boggs 1240 suggest at least a three-fold increase in reserves over the average vertical well will be realized. Assuming production decline similar to that of its offsets, the Boggs 1240 well will only recover approximately 200 MMcf in 35 years. This is far short of the 394 MMcf it would need to recover to be considered an economic success at a non-research cost of $500,000. However, the slant well may not decline as offsetting vertical wells have. Insofar as the slant well's drainage area will be highly elliptical relative to the vertical wells, there may be significant reason to expect accelerated recovery of gas in place and greater reserves than are initially apparent (A. Yost, II, personal communication). More production data is needed before any truly definitive statements regarding reserves and future performance of the Boggs 1240 can be made, however.

V. SUMMARY AND CONCLUSIONS

This paper presents the preliminary results of a recent directionally-drilled Devonian Shale well in Roane county, West Virginia. Drilling operations resulted in a wellbore which meets virtually all design criteria. Funds budgeted for the project totaled $656,000. Total funds expended for the project are approximately $680,000; a budget variance of less than 4%. Based on the above it is clear that the project has successfully demonstrated the technological feasibility of slant well drilling.

An economic model has been presented which suggests that risks associated with fracture distribution and gas recoverable from individual fracture zones can render a directional drilling program uneconomical. This result leads to the conclusion that careful site selection and well design will continue to be extremely important in future directional drilling applications in the Devonian Shale.

The economic success or failure of this project well is, as yet, uncertain. Whatever the final outcome of this particular well, it must be realized that fracture distribution and, hence, total recoverable reserves are random variables. Consequently, the efficacy of directional drilling at cost-effective reduction of risks associated with these variables can only be evaluated after many more such wells have been drilled.

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Eastern Gas Systems Analysis: Devonian Shales -- Tight Sands

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SUMMARY

Eastern Gas Systems Analysis studies are being performed at the Morgantown Energy Technology Center (METC) to determine the conditions under which gas produced through application of advanced technologies is economically attractive for selected residential, utility, commercial, and industrial markets. For advanced technologies such as horizontal drilling in the Devonian shales, these conditions are determined through the use of geologic screening and computer simulations of gas production, reservoir stimulation design, and economic-risk analysis. A major strength of the computer simulations is the use of probability distributions to address uncertainty. METC is also developing a market analysis methodology for advanced technologies. These areas are being examined to support the horizontal well technology and unconventional gas resource projects under the DOE Fossil Energy Program.

In addition to Devonian shales, METC is currently evaluating a tight gas-in-place (GIP) estimate of eastern tight gas sand formations in the Appalachian Basin. These formations include the Berea, Big Injun, and Benson sands in West Virginia and the Clinton (Medina) sands in Ohio. The tight GIP estimate of the eastern United States has been estimated to be 238 trillion cubic feet (Tcf). METC's current GIP estimate for the West Virginia formations is approximately 20 Tcf. A personal computer version of the Tight Gas Analysis System, TGAS, was used to complete this analysis. Currently, the gas price required to economically recover gas in these formations exceeds $2.06 per thousand cubic feet (Mcf), the wellhead price of gas for the Appalachian area. This work is being extended to the bordering states of Virginia, New York, Kentucky, and Pennsylvania to complete the assessment of these formations in the Appalachian Basin. Since the TGAS work is based on vertical well performance, future work will also address advanced technologies, such as horizontal wells, as a possible solution to make these formations economically feasible through expected increases in gas production.

In the area of advanced technology economics, METC has developed a simulation methodology that determines the probability distribution of horizontal well costs required to achieve a given target rate of return (ROR). This methodology requires probability distributions for variables such as gas price, gas production, and ROR. A risk analysis model samples these distributions and analyzes the well cost to achieve the input ROR values. This analysis is accomplished through an internal user-developed cash-flow model that yields a probability distribution of well costs. This model is being utilized to help provide guidance in planning and design efforts on DOE horizontal well projects.

METC's current stimulation modeling efforts are focused on developing a simplified, multi-crack, hydraulic fracture model for the evaluation and analysis of horizontal well stimulations. Based on the model analysis,

several conclusions provide insight into the factors governing multiple fracture propagation. In addition, a methodology is being determined to predict the performance of various stimulation types in the Devonian shales. A forecasting methodology is discussed that addresses the uncertainty, and determines the risks, of various stimulation methods applied to Devonian shales. This methodology will be used as a tool for forecasting the risks of various stimulation types prior to drilling and completion of Devonian shale wells.

BACKGROUND INFORMATION

Tight Gas Sand Analysis

Most oil and gas production in West Virginia and the central Appalachian Basin originates from formations of the Mississippian- and Devonian-age systems. These include Devonian shales and a series of tight gas sands. The tight gas sand formations currently being evaluated comprise inter-bedded sands, silts, shales, and limestones (Figure 1) and include the Clinton, Berea, Big Injun, and Benson sands. Tight areas (0.1 mD or less) are being evaluated. In 1982, the West Virginia Tight Formation Committee designated and developed maps of tight formations in West Virginia, according to the Federal Energy Regulatory Commission (FERC) guidelines issued in 1981. This study is based on reservoir and well data from these tight areas in West Virginia and the Clinton sands of Ohio. The purpose is to determine their future gas resource/reserve potential. Future work will be extended to bordering states in order to develop an appraised tight gas potential for the entire Appalachian Basin.

TGAS was developed under DOE/GRI sponsorship by ICF Resources Incorporated to aid in evaluating the production and the

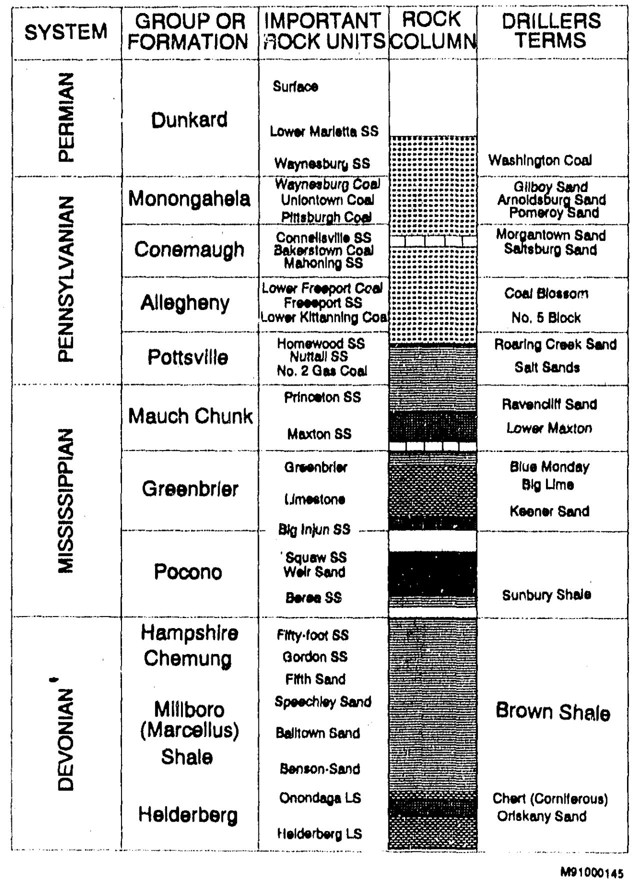

Figure 1. Generalized Geologic Column for West Virginia

economics of tight sand prospects. TGAS incorporates four analysis modules:

- **Resource Data and Geology Model**: calculates a total resource-in-place for the formation from volumetric reservoir data, including formation thickness, areal extent, porosity, reservoir pressure, temperature, and water saturation.

- **Technology Performance Model**: uses formation permeabilities and stimulation technology to determine the technically recoverable resource.

- **Engineering and Costing Model**: calculates the cost of drilling, completion, stimulation, and operating.

- **Exploration and Development Model**: considers the impact of advancements in drilling and stimulation technology.

Stimulation Modeling for Horizontal Wells

Current Eastern Gas Shales research efforts are focusing on the drilling and production of horizontal wells in the Devonian shales throughout the Appalachian Basin. Horizontal wells are thought to be necessary in formations with low permeability such as the Devonian shales to increase natural gas recovery and to reduce the risk of drilling a dry hole. With recent advances in drilling technology, horizontal and inclined wells are becoming popular in naturally fractured formations. In a horizontal weli, the borehole crosses multiple natural fractures in the reservoir, providing direct wellbore connection with high permeability gas flow networks. The permeability of these flow networks can be increased by stimulating the natural fracture system with non-damaging, proppant-laden hydraulic fracture fluids.

Although stimulation technologies such as hydraulic fracturing of vertical wells have been widely used in the gas industry over the last 30 years, information on stimulation of horizontal wells is scarce. Successful development of horizontal well technology for Devonian shales requires a thorough knowledge of stimulation treatment design. Stimulation of a horizontal well involves simultaneous propagation of multiple fractures from the wellbore. In order to reduce economic risks, it is necessary to develop reliable stimulation design tools for horizontal wells. The goal of this research effort was to review available data gathered from field projects, and to evaluate the applicability of a simplified model for predicting the performance of horizontal well stimulation in the Devonian shales.

Probabilistic Analysis of Horizontal Well Costs

Economic analysis of well projects after drilling, completion, and years of gas production, typically involves a before or after tax cash-flow model. The model calculates profitability in terms of net present value (NPV) and ROR. Data or variables needed for the analysis include gas price, annual production (from simulation or actual data), well costs, and operating costs. Results include ROR, NPV, and payback times. Most economic models are based on point estimates of the input and output variables. This method does not allow for uncertainty or risk, which should be quantified in order to provide a more informed analysis. Risk analysis takes judgements supported with actual data and translates them into the language of probability. The mathematical models used to perform risk analysis utilize Monte Carlo simulation to randomly sample data from probability distributions. The judgements and the data input as probability distributions represent concepts of the risks involved for a project. The following steps are followed to quantify the risk and uncertainty when analyzing horizontal well costs using simulation techniques (Newendorp 1975):

- Gather data,
- Isolate key variables,
- Quantify key variables,
- Apply concepts of uncertainty at the variable level,
- Enter input into a model, and
- Express the results.

PROJECT DESCRIPTION/RESULTS

Tight Gas Analysis of the Eastern Tight Gas Sands

In order to determine the potential gas resource available in eastern tight gas sand formations, TGAS was used to evaluate the gas production and economics of tight sand formations. The Appalachian Basin formations in this evaluation included the Clinton, Berea, Big Injun, and Benson sands.

The Clinton Sands are considered to be a complex network of off shore bars, distributary channels, shoals, and delta front sands enveloped by marine shales. Hydrocarbon production is limited to eastern Ohio, western New York, and northwestern Pennsylvania. In eastern Ohio, the economically important sandstone units within the Clinton are the Grimsby and Cabot Head sands, or the Red and White Clinton, respectively. The net pay of this sand ranges from 7 to 60 ft, porosity ranges from 5 to 13%, and effective permeability averages 0.1 mD. The Clinton is considered a tight reservoir, with wells capable of producing 500 million cubic feet (MMcf) of gas during a productive life of 15 to 25 years. The source of these data included reports prepared by C.F. Knutson (1984, 1986). Data included log data, net pay, porosity, gas saturation, and permeability. Additional data were obtained from an independent Ohio gas and transmission company, the Ohio Division of Oil and Gas, and the State of Ohio Department of Natural Resources.

The lower Mississippian Pocono Group "Big Injun" horizons consist of lense-shaped and inter-fingered sandstones, siltstones, and shales. The high lateral variability is characteristic of fluvial and deltaic environments. The term Pocono Big Injun is usually confined to the sandstone units of the uppermost Pocono Group, lying below the Maccrady Formation. The Big Injun thickness ranges up to 200 feet (Ameri and Aminian 1988).

The Berea Sandstone in West Virginia is defined as the basal sandstone unit of the early Mississippian-Pocono Group. It is a persistent sandstone-siltstone unit in the subsurface throughout the western half of the State and extends into eastern Ohio, Michigan, western Pennsylvania, and Virginia. Fluvial and marine environments have been proposed as the origin of the Berea Sandstone. Production has been primarily from two linear sandstone units: (1) the Gay-Fink Channel and the Cabin Creek Channel in the central part of the state, and (2) marine sands in western counties.

The Benson sand is Upper Devonian in age, consisting of very fine-grained sandstone, siltstone, and shale. The Upper Benson is the principal gas reservoir. Porosity is usually less than 14% and averages 5 to 10%. Permeability varies from 0.1 to 2.0 mD.

A summary of reservoir parameters used in the analysis of the eastern tight sand formations is shown in Table 1. Using an input gas price of $2.00/Mcf, TGAS calculates a resource gas-in-place value along with technically and economically recoverable gas estimates. A resource estimate of 18 to 20 Tcf was determined, based on the reservoir data available for the eastern tight formations. However, based on the $2.00/Mcf gas price, the formations do not show economically recoverable gas. Advanced technologies, such as horizontal wells, may be able to increase the gas production from these areas, creating a potential for economically recoverable gas.

Stimulation Modeling for Horizontal Wells

Fractured Devonian Shale Risk Analysis: METC numerical modeling efforts have focused on developing a simplified multi-crack hydraulic

Table 1. TGAS Summary of Reservoir Formation Properties

Property	Clinton	Big Injun	Berea	Benson
Permeability (mD)	0.068	0.10	0.10	0.10
Total Porosity (%)	8.9	9.9	7.2	9.5
Net Pay Thickness (ft)	15.0	17.0	12.0	6.7
Depth (ft)	4325	2025	2890	4393
Pressure (psi)	1260	505	543	1327
Gas In Place (Tcf)	1.2	6.7	4.7	5.7

fracture model for evaluation and analysis of horizontal well stimulations. This model is based on the assumption that individual fracture propagation is governed by the theory presented by Geertsma and deKlerk (1969) for single vertical fractures of a constant height. It was also assumed that the flow rate in each fracture will not change significantly during the stimulation treatment. A schematic of the stimulation process being modeled is shown in Figure 2. Prior to analysis of the field project data, the model was evaluated by predicting a number of cases involving multiple fracture propagation. Based on the model analysis, several conclusions provide insight into the factors governing multiple hydraulic fracture propagation:

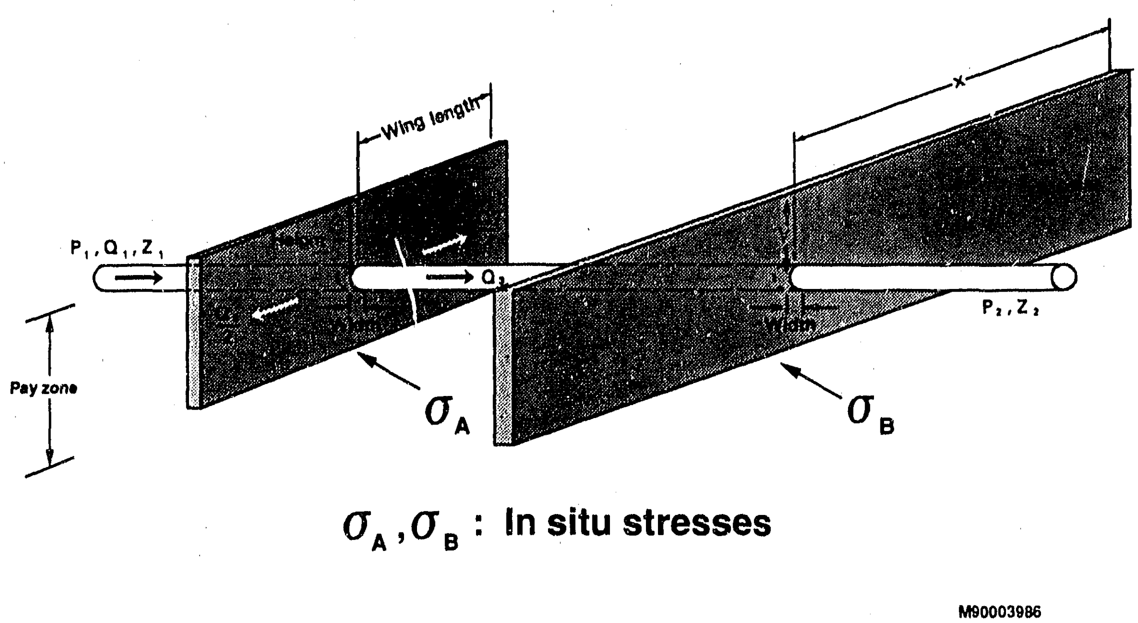

Figure 2. Schematic of a Multiple Fracture System in a Horizontal Well

- Both turbulent and laminar conditions of flow exist in different segments of the wellbore.

- Entry losses into the natural fractures from the well have a significant influence on the propagation of a multiple fracture system.

- Fracture inclination to the wellbore has a significant influence on the propagation of a multiple fracture system.

METC recently sponsored a field research project to investigate the recovery efficiency of multiple hydraulic fractures induced in a horizontal well in the Devonian shale. Details of the Recovery Efficiency Test (RET) project can be found elsewhere (Overbey, Yost, and Yost 1988). The field test site selected for the RET project is in Wayne County, West Virginia. The objective of the RET stimulation test was to evaluate how varying fluid types, volumes, rates, pressures, and proppants affects stimulation treatments in a horizontal well. Eight zones were isolated along the horizontal portion of the well, and seven hydraulic fracture treatments were performed in six of the eight zones. A liquid carbon dioxide stimulation (Treatment No. 4) was performed on zone 1. The data gathered from this treatment were used to evaluate the predictive capability of the developed multi-crack hydraulic fracture model for horizontal well stimulation analysis. Three cases were considered with the multi-crack model to evaluate Phase 1 of Treatment No. 4. Details of these cases, which depict variations of probable fracture inclination and fracture location along the wellbore, are shown in Table 2.

Table 2. Fracture Analysis Summary -- Wayne County Horizontal Well

Fracture Identification	Measured Distance (ft)	X-coord. (ft)	Fracture Orientation (Degrees) Case 1[1]	Fracture Orientation (Degrees) Case 2	Fracture Orientation (Degrees) Case 3
1	5682	64	76	86	85.3
2	5677	69	86	86	86.5
3	5675	71	86	86	86.0
4	5670	76	86	86	85.0
5	5665	81	86	86	85.0
6	5658	88	86	86	85.0
7	5639	107	86	86	81.7
8	5632	114	86	86	85.0
9	5626	120	86	86	83.0
10	5614	132	86	86	81.5

[1] Based on RET results

For case 3, fracture inclinations were varied to back-calculate fracture flow rates that compared favorably with the trend measured from the tracer logs. Computed flow rates in individual fractures for these three cases are shown in Table 3. Figure 3 compares predicted fracture flow rates for case 3 with those measured from tracer logs. Predicted and measured fracture injection rates are in good agreement when the fracture inclinations are slightly adjusted. As more field data are gathered and the multiple fracture model is modified and improved, additional comparisons will be made. These analyses will provide further insight into the factors that govern multiple hydraulic fracture propagation in horizontal wells.

Risk Assessment for Devonian Shale Stimulation: Simulation is required for economic gas recovery from low permeability Devonian shale reservoirs. In the past, various forms of stimulation have been applied and analyzed, including explosive shooting, tailored pulse loading, and hydraulic fracturing with foam or carbon dioxide cryogenics. Statistical, test site, and qualitative evaluations of these technologies have been conducted using production and stimulation treatment data (Horton 1981). Analysis of pre- and post-stimulation data has also been performed (Lancaster 1988). Various reservoir properties and mechanisms that impact the efficiencies of different stimulation types have been identified from these studies. These include damage of the shale by hydraulic fracturing fluids, reservoir in-situ tectonic stress, capillary pressure effects, hydraulic fracture fluid clean-up capability, fracture proppant concentrations and conductivity, and created fracture geometry.

Table 3. Stimulation Flow Rates -- Wayne County Horizontal Well

Fracture Identification	Average Flow Rate based on tracer log analysis (BPM)[1]	Average Computed Flow Rate Case 1 (BPM)	Average Computed Flow Rate Case 2 (BPM)	Average Computed Flow Rate Case 3 (BPM)
1	0.35	9.3	1.0	0.395
2	0.17	0.1	1.0	0.365
3	0.17	0.1	1.0	0.455
4	0.59	0.1	1.0	0.580
5	0.59	0.1	1.0	0.595
6	0.55	0.1	1.0	0.685
7	2.38	0.1	1.0	2.205
8	0.55	0.1	1.0	0.660
9	1.44	0.1	1.0	1.300
10	3.33	0.1	1.0	2.980

[1] Barrels per minute

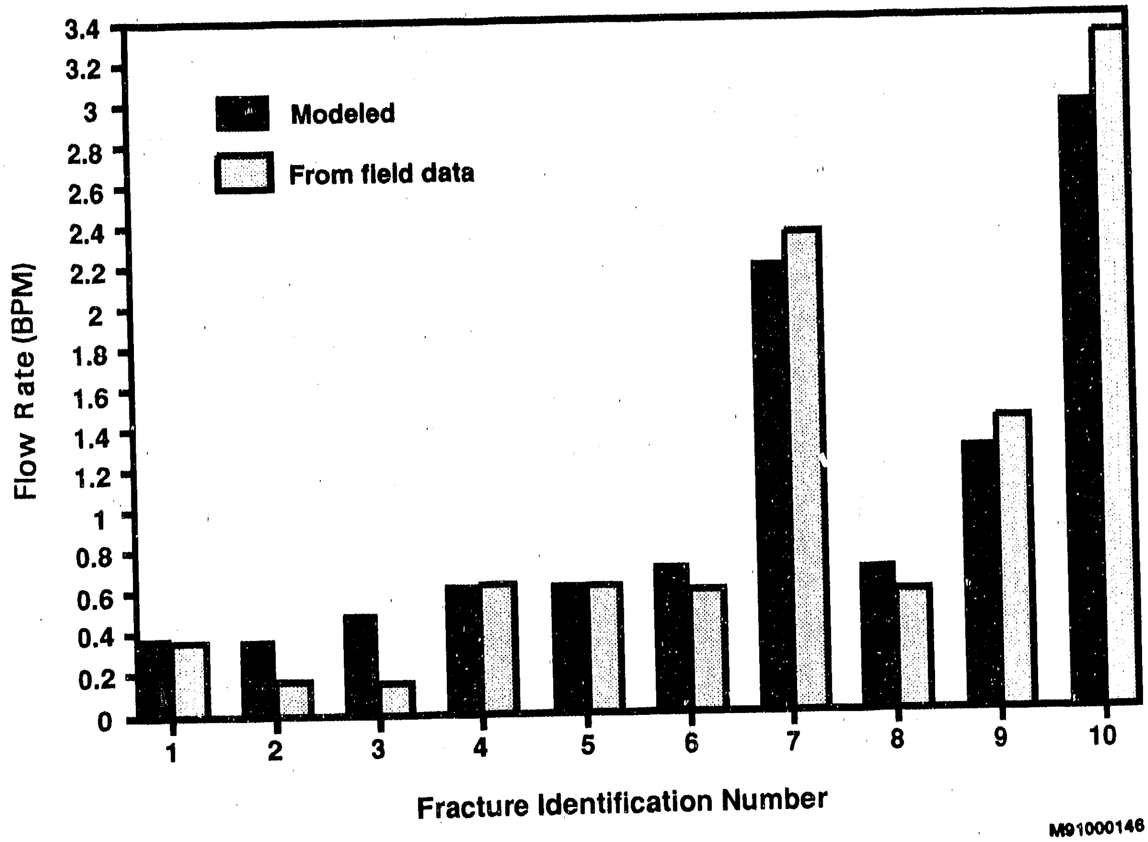

Figure 3. Comparison of Modeled and Measured Fracture Flow Rates -- Zone 1, Wayne County Horizontal Well

Current METC modeling efforts are focused on predicting the performance of various stimulation types in the Devonian shales. This forecasting methodology will determine risks and rewards of various stimulation types in areas of Devonian shale exploration and development. Stochastic risk analysis will consider environmental impacts, economic constraints, geologic and reservoir properties, and stimulation treatment types. Numerical models are used to predict fracture geometries and reservoir responses from selected stimulation treatment variables. These predictions provide the information required to evaluate stimulation performance for historical, measured, or estimated reservoir conditions. Ultimately, this methodology will provide a tool for forecasting the risks and rewards of various stimulation types prior to drilling and completion of a Devonian shale well.

Probabilistic Analysis of Horizontal Well Costs

In order to probabilistically examine the well costs associated with horizontal drilling in eastern Devonian shale, the first step was to develop an after-tax cash flow model for use in the PRISM risk-analysis-and-modeling software package. The cash flow model includes severance taxes, West Virginia state taxes, and federal taxes, along with royalties and operating costs. Simulated production data from the DOE Putnam County, West Virginia, horizontal well project served as input production data for the cash flow model. Probability distributions were assigned to the following input variables used in the cash flow model: gas price, initial production rate, pay thickness, and porosity. Timing trends were also included with the gas price and initial gas production distributions to account for gas price inflation and the decline rate of the well over the 10-year life of the study. Compared to most economic analyses in which ROR is an output, this analysis uniquely assigns an input probability distribution to ROR, with the output being a distribution of required well costs to meet the target ROR. The ROR distribution selected by the user is based on profitability requirements for attractive economics. ROR is calculated through an iterative method, solving for the interest rate (i), which results in capital investments and discounted cash flows summing to zero over the life of the project:

$$\sum_{j=0}^{L} \frac{NCF_j}{(1+i)^j} = I_0 ,$$

where NCF = Net cash flow, j = Time period, L = Total time (years), I_0 = Initial investment at time zero, and i = Interest rate in percent.

In this study, ROR was an input distribution with a most likely value of 20% (Figure 4). The output distribution of well costs is shown in Figure 5. The expected or most likely result is the well cost required to obtain a ROR of 20%. Higher input RORs would show lower well cost requirements. In order for a project to have a higher ROR, the well costs must be reduced. The amount of gas produced, gas price, and well costs all have an influence on ROR. This analysis can also identify which of these factors has the best chance of increasing a projected ROR. This is accomplished through a sensitivity analysis using different ranges for respective distributions. These results will be very useful in the planning and design efforts for future horizontal well projects.

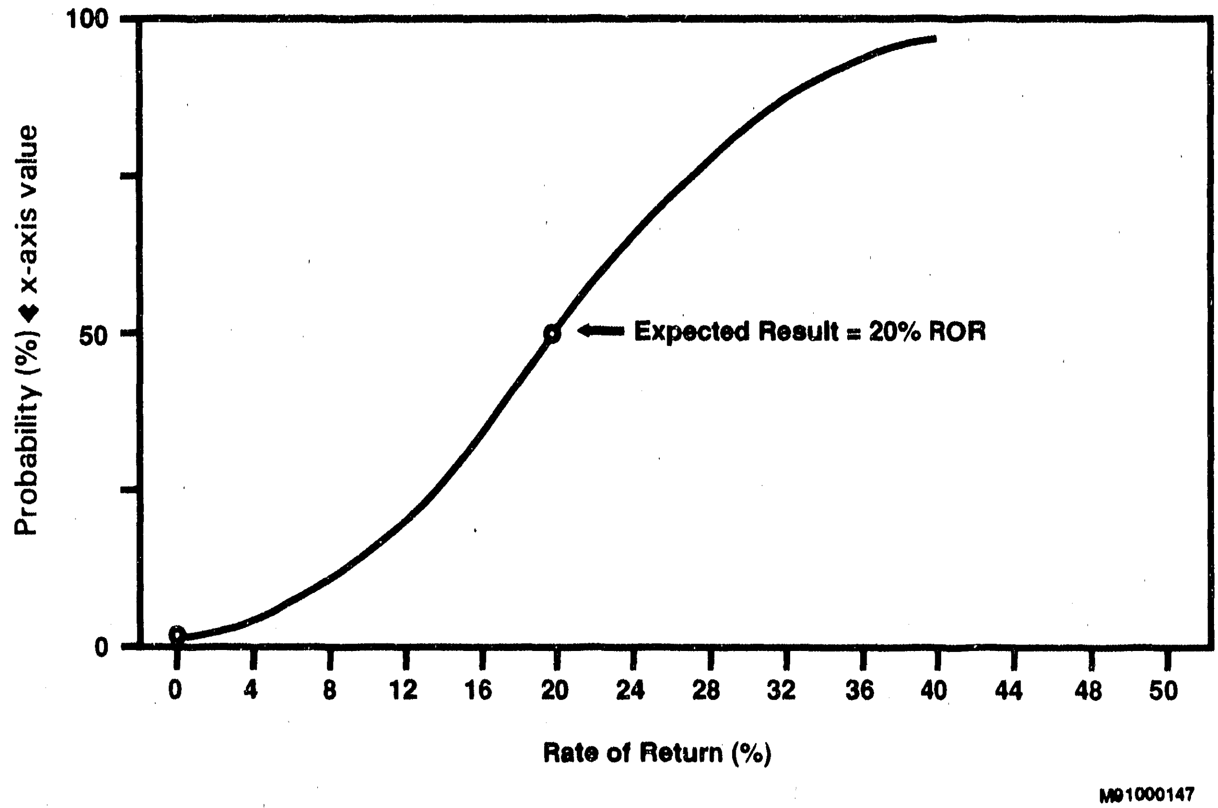

Figure 4. Probability Distribution of the Rate of Return

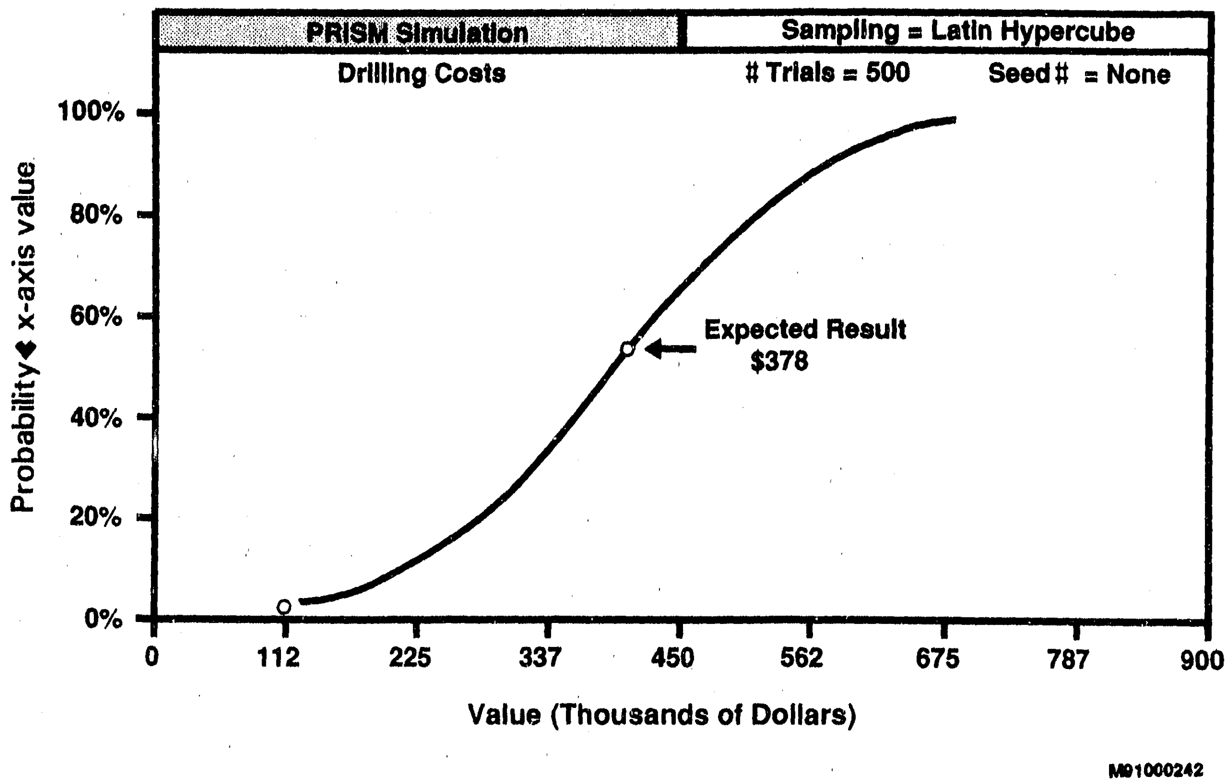

Figure 5. Probability Distribution of Well Costs

CONCLUSIONS

- The preliminary tight gas potential of the eastern tight gas formations in West Virginia and Ohio is estimated to be 18 to 20 Tcf.
- A simplified, multi-crack hydraulic fracture model enhances the understanding of multiple fracture propagation from horizontal wells.
- Risk assessment is a valuable aid in the planning and design of horizontal wells from both a well-cost and stimulation perspective.

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Session 3

Conventional/Speculative Resources

Deep Gas

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ABSTRACT

Deep gas research emphasizes studies of natural gas in subduction emplaced sediments and in deep sedimentary basins. Central to the subducted zone research is the hypothesis that natural gas is generated in sediments carried to great depths, providing a deep gas source and potentially providing source gas to shallower, drillable traps through deep fracture systems. Early in the project, the Cordilleran Geologic Province was selected as the prime area for study because of its modern (active) and fossil (inactive) subduction zones. Although many areas of North America appear to have experienced convergent plate tectonic activity in past geologic times, the western Cordillera contains thrust fault structures that may have enabled deep emplacement of hydrocarbon-generating sediments during more recent geologic ages (the last 180 million years). The specific area of interest in this province encompasses approximately 1.5 million square miles of the western U.S. (including Alaska) and Canada; other portions of this same province extend southward into Mexico and Central and South America.

For subduction-emplaced sediments, ongoing research consists of basic studies of hydrocarbon generation, stability, and preservation at depths in excess of 15,000 feet, and a comprehensive evaluation of the geologic structures, stratigraphy, and geochemistry of the above region.

Results to date include (1) geologic and geophysical evidence of deeply emplaced sedimentary rock units at depths exceeding 30,000 feet in western Washington and south-central Alaska, and high-resolution, seismic-reflection verification of structures defined by reconnaissance geophysics (gravity, magnetic, and magnetotelluric techniques) in western Washington; (2) a new methodology for verifying deep methane stability with fluid inclusion studies; and (3) a preliminary gas resource estimate of 3,000 trillion cubic feet.

Deep gas research in deep sedimentary basins is focused initially on deep reservoir questions of porosity and permeability preservation, hydrocarbon generation and preservation, and migration pathways in high-ranked deep basins of the U.S.

Gas Hydrates

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ABSTRACT

Gas hydrate research is a part of the Unconventional Gas Recovery (UGR) Program, a multidisciplinary effort that focuses on developing the technology to produce natural gas from resources that have been classified as unconventional because of their unusual geologies and unique production mechanisms. The approach to developing the necessary knowledge and understanding of gas hydrates consists of ongoing efforts that emphasize geological studies; characterization of the resource; and supporting research which includes modeling of reservoir conditions, production concepts, and predictive strategies for stimulated wells. Complementing this work, research also focused on understanding the in-situ detection of hydrate deposits and, ultimately, field tests to verify extraction methods.

Private funding for gas hydrate research and development (R&D) is insufficient for several reasons: (1) the producibility of gas hydrates as an energy source is still unknown, (2) the immediate and future gas requirements are expected to be constant, and (3) the U.S. still relies heavily on imports. The U.S. DOE is providing leadership for research in gas hydrates and is coordinating its activities with academia, industry, private groups, Federal agencies, and their foreign counterparts. In response to this need, the DOE's Morgantown Energy Technology Center (METC) implemented a gas hydrate R&D program that emphasizes an understanding of the resource through (1) an assessment of current technology, (2) the characterization of gas hydrate geology and reservoir engineering, and (3) the development of diagnostic tools and methods. Recovery of natural gas from gas hydrates will be made possible through (1) improved instrumentation and recovery methods, (2) developing the capability to predict production performances, and (3) field verification of recovery methods.

In pursuit of these efforts, the gas hydrate research project is made up of three technical elements and a project management function. The project management function is a DOE function of planning, execution, control, and technical integration of the project. Each of the technical elements is described here:

- **Geologic Research** -- Activities in geologic research have been focused on mapping, characterization, and analyses of geological deposits existing within the hydrate stability zone in both onshore and offshore areas. These studies are being undertaken to determine the factors that permit or prohibit the formation of gas hydrates in the geological environment. This geologic analysis will generate data to guide more detailed, site-specific research required for the development of reservoir diagnostics, stimulation design, and eventual estimates of gas hydrate reserves.

FY 91 research in this category focuses on the analyses of geologic, water, and gas samples collected from Alaska's North Slope and on the completion of offshore analyses of suspected hydrate deposits.

- **Generic Research** -- Generic research is generally limited to laboratory studies defining the fundamental properties of gas hydrates through both prior year and current year funds. These studies, along with both geophysical and geochemical analyses, will provide the necessary data to identify features that can aid industry in locating and defining the gas hydrate reservoir geometry.

  FY 91 activity in this research category focuses on integration of data as it becomes available and will initiate analysis of reservoir characteristics. Work will continue on evaluation of subsidence potential in areas of hydrate dissociation and production.

- **Production Research** -- Modeling research is limited to thermal injection. Research focuses on model development for hydrate areas associated with high-viscosity hydrocarbons. Laboratory experiments are performed as required. Preliminary development of a hydrate-production well design has also been undertaken.

Accomplishments in FY 90 include the following activities and results:

- The completion of all 14 basin reports and the final report on the geological evolution and analysis of offshore gas hydrate deposits.
- Gulf of Mexico seismic profiles indicate significant gas seepages, which may have a direct bearing on gas hydrate deposits.
- Gas shows in North Slope wells have been at both the top and bottom of the suspected hydrate horizons, and two wells in Prudhoe Bay (Z-8 pad) had significant gas shows at four, preselected, hydrate-deposits horizons.
- Gas hydrate estimates for the onshore Prudhoe Bay/Kuraruk area have been increased from 11 to 14 trillion cubic feet.
- Preliminary identification of gas hydrates has been made in the Barrow Gas field area.
- Seismic mapping has been initiated in the Blake-Bahama region of offshore North and South Carolina.

Infield Reserve Growth/Secondary Natural Gas Recovery: Targeted Technology Applications for Infield Reserve Growth - Year Two Report

CONTRACT INFORMATION

Contract Number	DE-FG21-88MC25031
Contractor	Bureau of Economic Geology The University of Texas at Austin University Station, Box X Austin, Texas 78713 (512) 471-1534
Contractor Project Manager	Robert J. Finley
Principal Investigators	Robert J. Finley Edgar H. Guevara Raymond A. Levey
METC Project Manager	Gary V. Latham
Period of Performance	September 1, 1988 to August 30, 1991
Schedule and Milestones	

FY 1990 Program Schedule

	S O N D J F M A M J J A
Task 1.0 Methodology for Choosing Study Areas (Carbonates) (Task 1.0 completed for Sandstones)	
Evaluation of Operator Activity	
Initial Simulator Configuration	Not initiated for carbonates
Initial Field Screening	
Refined Field Screening	Not initiated for carbonates
Task 2.0 Untapped Compartments: Integrated Characterization of Candidate Reservoirs (Sandstones)	
Geological Characterization	
Development of Cross Section Frameworks	Completed

	S	O	N	D	J	F	M	A	M	J	J	A
Mapping of Target Reservoirs												
Engineering Characterization												
Task 3.0 Formation Evaluation for Bypassed Gas Zones												
Geological Support for Formation Evaluation												
Sample Analysis for Shaly Sandstone Evaluation												
Task 4.0 Interwell Extrapolation and Related Deeper Pools												
Subregional Stratigraphic Analysis												
Field-Scale Analysis of Deeper Play Components	No activity											

OBJECTIVES

In the last decade, characterization of the internal geometry of reservoirs, mainly oil reservoirs, has demonstrated a higher degree of compartmentalization than previously recognized. This compartmentalization is primarily a function of the depositional system and, secondarily, of the structural and diagenetic history of the reservoir after deposition. The objective of this project is to define the potential for incremental gas recovery based on better understanding of depositional and diagenetic heterogeneity within known nonassociated gas reservoirs. Where significant geologic variation occurs, untapped or bypassed reservoir compartments remain to be drained of natural gas by drilling or recompleting strategically placed development wells. Deeper pool potential, which is closely related to producing depositional systems, can be better defined by sequence stratigraphy and also offers opportunities for increased reserves. However, because deeper pool drilling is part of standard industry practice more related to exploration than development, it is not a major focus of this project.

Approaches to defining the distribution of unrecovered resources by depositional system and methods for maximizing their recovery are being developed and tested as part of the Infield Reserve Growth/Secondary Gas Recovery (SGR) Project. This project, a joint effort of the Gas Research Institute (GRI), the U.S. Department of Energy (DOE), and the State of Texas, is focused specifically on Texas natural gas reservoirs as a major subset of the Nation's natural gas resource base.

Results of this project will better enable producers to economically recover this discovered but undeveloped natural gas resource through integrated geological, engineering, petrophysical, and geophysical assessments. Depositional systems studies of major gas reservoirs in South Texas have already indicated the complexity of fluvial-deltaic reservoirs in the Frio Formation; thus, Frio reservoirs have become a major target for demonstrating improved recovery potential in sandstones. A second target will include heterogeneous carbonate reservoirs either in East Texas or in the Permian Basin of West Texas.

BACKGROUND STATEMENT

To date, the project has operated primarily in four fields in the Gulf Coast Basin that produce from different formations under different conditions of depth, pressure, and permeability. Primary emphasis has been on non-geopressured, conventional permeability reservoirs like the Frio Formation in Seeligson and Stratton fields. These reservoirs were deposited as part of a bedload-rich fluvial system that fed a major deltaic depocenter in South Texas. The geopressured, low-permeability reservoirs of the Vicksburg Formation were the objective of studies of deltaic reservoirs at McAllen Ranch field, also in South Texas. Reservoirs of the Wilcox Group in Lake Creek field in the northern part of the Texas Gulf Coast Basin include fluvial-deltaic gas reservoirs that vary from conventional to low permeability.

Cooperative data collection with operators drilling development wells has occurred in all these fields. Considerations of geology, amenability to engineering testing, depth, and cost indicate that the Frio Formation will be most appropriate for drilling of a project-operated Field Experiment well to confirm or challenge concepts developed during cooperative data collection, and to test current state-of-the-art and newly developed technologies in an integrated manner. It is anticipated that the Field Experiment well for sandstones will be drilled early in 1991.

PROJECT DESCRIPTION

Bypassed Reservoirs

Significant emphasis of the project to date has been on bypassed gas in sandstone reservoirs; a second phase of the research will deal with carbonate reservoirs. Where contemporaneous subsidence and deposition of dominantly fluvial sandstone reservoirs has taken place, 30 (or more) vertically stacked reservoirs have been deposited, as in the Frio Formation of South Texas. Not all of these have been fully drained, particularly those in which sand-rich fluvial axes are separated by floodplain mudstones and poorly interconnected crevasse splay deposits.

For this project, engineering pressure testing and an advanced cased-hole logging suite are being applied in conjunction with geological modeling to fully characterize the interwell area. This modeling better defines the interconnection of producing facies and incorporates engineering assessments of pressure histories and production decline rates. Drilling of new wells to deeper targets in the field being studied allows open-hole pressure testing to be used to define unrecovered gas in bypassed compartments. Core has defined diagenetic heterogeneities for calibration of open-hole and cased-hole logs and has shown that channel margins, because of either channel lag material or cementation, may have lower permeability than the bulk of the fluvial sand body. The overall result will be a fully integrated reservoir analysis that can be used to define the distribution of bypassed gas.

Untapped Compartments

Depositionally heterogeneous reservoirs are likely to have untapped compartments where wells have been sited largely on the basis of spacing rules or for protection against drainage along lease boundaries rather than on geologic variation. A key question for this study is whether natural gas, having lower viscosity than oil, is subject to incomplete recovery due to reservoir heterogeneity. Evidence suggests that heterogeneity within the 320- to 640-acre spacing typical of many gas reservoirs with conventional permeability allows for untapped and incompletely drained compartments in heterogeneous depositional systems.

Data and interpretations made during the initial investigation of bypassed gas are being used in developing reservoir models necessary for targeting untapped compartments. Defining component facies from abundant well data within gas-bearing depositional systems containing bypassed gas is a key first step in assessing (1) the degree of continuity of reservoir types between wells, (2) the relationship between reservoir size and the expected area of gas drainage, given specific reservoir quality parameters, and (3) the likelihood that undetected heterogeneities are affecting gas production. These heterogeneities, if sufficient barriers to flow, lead to untapped or incompletely drained compartments within reservoirs that can be predicted using geological, engineering, and geophysical approaches at the facies and reservoir scale. Geophysical techniques, especially vertical seismic profiling (VSP), reverse VSP, and cross borehole tomography, offer the prospect of more directly defining the geometry of target reservoir compartments.

Deeper Pool Potential

This project originally included evaluation of gas resources in deeper reservoirs that are closely related in depositional system to currently productive shallower reservoirs. However, industry has established approaches to such development, and the project Technical Advisory Committee has determined that deeper pool potential should be de-emphasized.

RESULTS

Results from the first 1.5 years of study indicate that both stratigraphic and diagenetic compartments affect natural gas recovery in sandstone gas reservoirs of the Texas Gulf Coast Basin. Variations in both the scale of heterogeneity and depositional environment of the reservoir system play an important role in gas reserve growth potential.

Scales of Heterogeneity: An Example From McAllen Ranch Field

Research efforts have focused on the overpressured Oligocene Vicksburg S-reservoirs of the Rio Grande Embayment. Stratigraphic and geophysical analysis of McAllen Ranch field identified a series of six deltaic sandstone intervals. Geologic interpretation of core and well logs from two cooperative wells (Shell Western E&P, Inc. McAllen Ranch B-17 and B-18) indicate facies heterogeneity and diagenetic boundaries across the field. Characterization of these reservoirs has been addressed through integrated petrophysical, engineering, and geological analyses.

Petrophysical Analysis. Confined sand-shale, overpressured sequences typical of deep Vicksburg reservoirs are ideal for formation evaluation research in shaly sands. Logging and coring programs on the cooperative wells provided a high quality data set to test shaly sand models using core analysis data to confirm log calculations. The logging program consisted of phaser induction, litho-density, neutron, gamma ray, digital long spaced acoustic, and wireline pressure tester logs. Approximately 240 ft of core from the "S sandstone" interval was recovered and measurements were made for restored state porosity, permeability, capillary pressure, cation exchange capacity, cementation and saturation exponents, x-ray diffraction analysis, and thin section analysis. Use of measured core water saturations to confirm log-derived water saturations is not commonly done, but an opportunity to do so existed here because the wells were drilled using oil-based mud.

Several water saturation models were evaluated and a Waxman-Smits model was used to make this comparison. Clay weight percent was taken from x-ray diffraction analysis and used as a basis to determine volume of clay from well log clay indicators. Cation exchange capacity (CEC) was determined by correlating measured CEC values with x-ray diffraction clay fraction. This allowed computation of a continuous CEC based on the log-core correlations. Porosity was calculated using a fixed grain density of 2.66 grams per cc. This allowed the best correlation to core porosity. Water saturations were calculated using the Waxman-Smits model with the log-derived CEC, cementation and saturation exponents taken from special core analysis, and a formation water resistivity supplied by the field operator.

Formation evaluation results show several important points. Capillary pressure measurements indicate core water saturation in some cases are too low. The initial mercury injection capillary pressure measurements performed by the operator in the sandstones show good general agreement. However, in the siltstones above the S-4 reservoir, water saturations are generally higher (up to 30 percent) than measured core water saturations. This is a significant difference but they are confirmed using measurements performed by Core Laboratories. Using the log derived values of porosity, and parameters taken from core analysis (CEC, m, n), calculated water saturations agree with the capillary pressure water saturations. The difference between these capillary pressure and measured core water saturations is being evaluated. Porosity and water saturations are displayed together with the results of the core analysis and raw log curves (Fig. 1). The capillary pressure water saturations are displayed using a common water level of 13,600 ft. The differences are easily seen. Agreement between log and core data are generally good, with the exception of the water saturation measurements.

Engineering Assessment. Engineering questions have been addressed that are unique to the character of the low-permeability, overpressured Vicksburg reservoirs of South Texas. While a tank-like, compartment model has been useful in assessing reservoir performance in the more permeable reservoirs (such as Stratton and Seeligson fields), this model has been shown to be inappropriate for McAllen Ranch reservoirs. Because of the low effective permeability of the reservoirs (~0.05 md), a low-permeability barrier (~0.0005 md) at distances on the order of 500 to 1,000 ft is not readily detectable in well behavior and performance represented by a tank-like model. Therefore, a two-dimensional, finite element model has been used to evaluate performance of hydraulically fractured wells in low-permeability reservoirs of the Vicksburg play like those in McAllen Ranch. The model provided accurate simulation of wells completed by hydraulic fracturing and applied the geologic reservoir model and the permeability-thickness and hydrocarbon porosity-thickness data derived from well log analysis. This simulation included five producing wells in a domain bounded in a wedge-shaped area by two intersecting faults. In addition to observed initial pressures in these wells, wireline pressure test results from three other wells were used to calibrate the model. A history match was achieved only by inserting a low-permeability barrier across a portion of the reservoir as indicated in the accompanying figure showing the finite element grid (Fig. 2). Thus, there is evidence for permeability barriers in McAllen Ranch reservoirs, but in view of low reservoir permeability these could only be potentially demonstrated by very long-term (years) well interference, and not by single well performance.

A principal hypothesis that has developed as part of the study of McAllen Ranch is that a creep-compaction drive mechanism plays a significant role in determining well performance. For example, it is observed that wells exhibit significant increases in production rates for a significant period following curtailment of production. This production phenomenon is attributed to time-delayed compaction, or creep, of the overburden as pressure support is removed by fluid production from the overpressured reservoir rather than to reservoir heterogeneity. Thus, porosity in the reservoir declines with time as the overburden slowly "flows" to re-establish mechanical equilibrium.

To demonstrate that creep-compaction can account for observed well behavior following curtailment, the finite element model was modified to simulate a time-delayed porosity decline determined by pressure history in each volume element. The resulting model exhibited behavior like that seen in the field.

Geological Heterogeneity. There are two potential sources at different scales for additional infield reserves in Vicksburg gas reservoirs of McAllen Ranch field. The most likely sources for additional completions are distributary channel-fill sandstones that are laterally discontinuous. Since sandstone intervals are stacked, recompletion opportunities are present, but age of wellbore tubular goods may make such recompletions technically difficult. Stacked distributary channels are prevalent in the proximal parts of deltaic, progradational intervals that make up lower Vicksburg reservoirs similar to the S reservoir. Therefore, in other gas fields, infill recovery efforts could target the proximal portions of deltaic packages where stratigraphic variability is highest. Areas laterally adjacent to the distributary channels (McAllen Ranch B-area) contain more continuous shoreface and delta front sandstones. This offers less potential for infill gas recovery and greater lateral continuity exists. Additional potential reserve growth is partially a function of completion practices. Single completions from numerous stacked sandstones assume there is a single drainage radius. Because the reservoir quality and resultant drainage radii vary among reservoirs and within a single reservoir resources may remain between wells in selected sandstones. This is one aspect of compartmentalization of the reservoir.

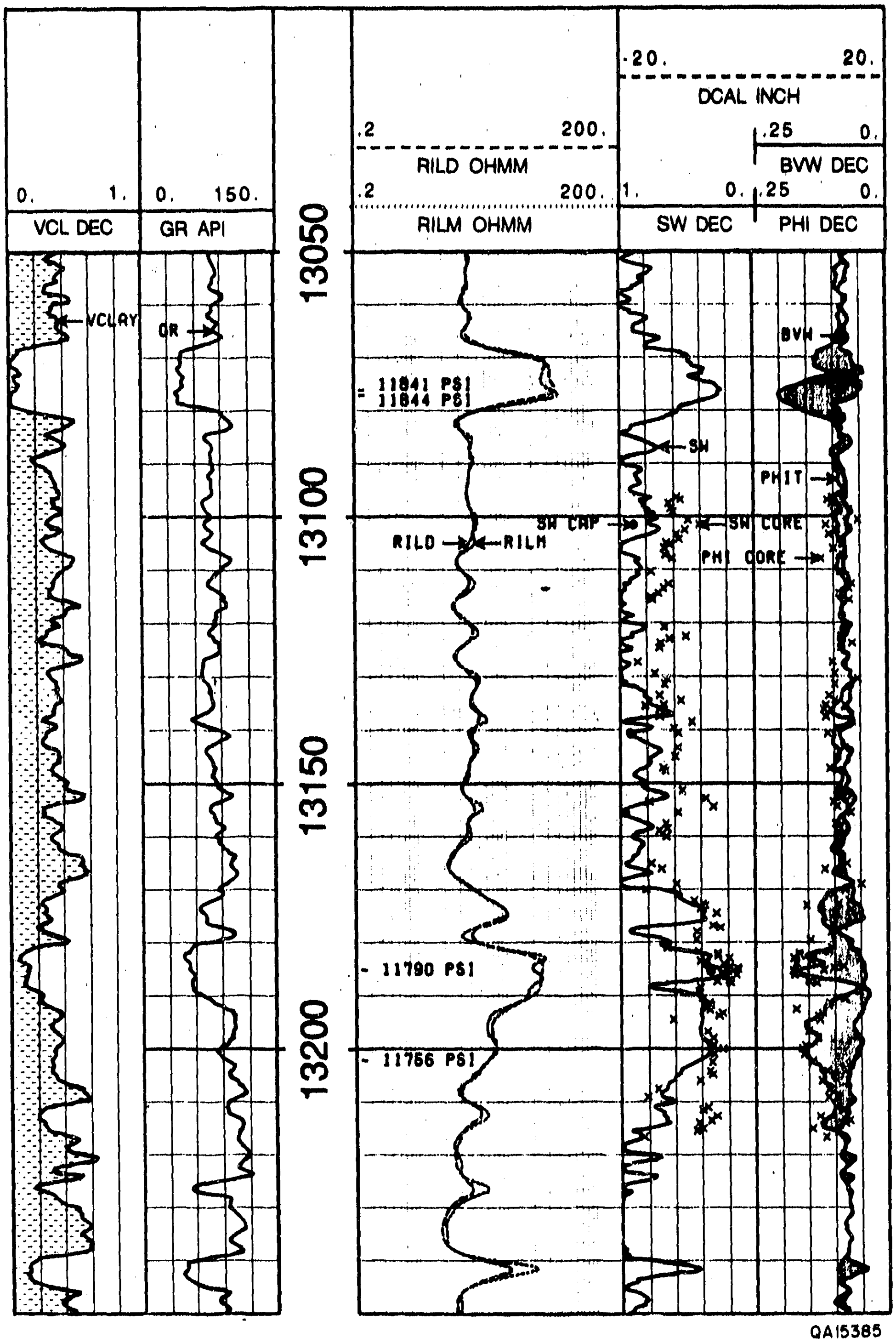

Figure 1. Comparison Of Core Analyses And Log Derived Properties From The Shell Western E&P, Inc. McAllen Ranch B-18 Cooperative Well.

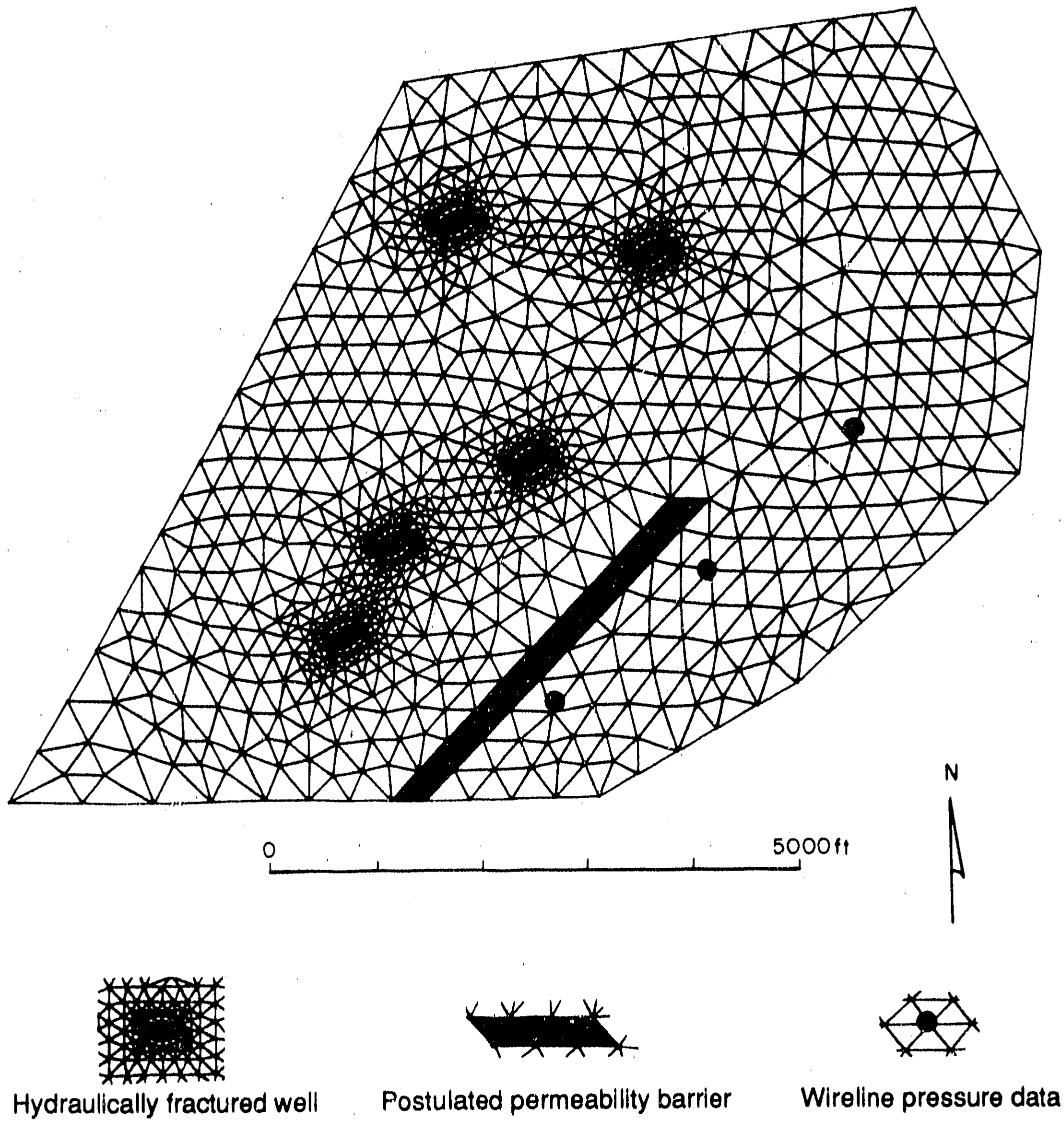

Figure 2. Two-Dimensional Finite Element Grid Utilized To Model The S-4 Reservoir In The B-Area Of McAllen Ranch Field.

The most important cause of variability in the S reservoir is diagenesis which creates variation in drainage radii for different sandstones in the same well. The development of secondary porosity within the S reservoir sandstones is the most important diagenetic control on reservoir volume and permeability. Large variations in porosity and permeability correlate with changes in diagenesis but not with depositional changes. Calculations of projected production and original gas in place indicate highly varying drainage radii. Recoveries based upon extrapolated rate decline data were compared with material balance projections based upon volumetric estimates of initial gas-in-place. Comparisons for seven wells in the S-4 reservoir indicate that significant variations between wells are seen, and that interpretation of results is strongly dependent on accurate estimates of initial water saturation and the assigned porosity cut-off that determines contributing reservoir volume.

Assessment of Facies Heterogeneity in Fluvial Reservoirs: Seeligson and Stratton Fields

Research on fluvial reservoirs has focused on the normally pressured Oligocene middle Frio reservoirs along the Vicksburg Flexure of South Texas. Lithologic and facies heterogeneity of middle Frio fluvial reservoirs are a function of changes in the stratigraphic architecture which can vary not only among different fields but within a single reservoir level of the same field. A spectrum of fluvial architectural styles has important implications for reservoir compartmentalization (Fig. 3). A variation from laterally stacked to vertically stacked channel systems was documented through closely spaced well log correlations across the 2,500-ft thick middle Frio section. High resolution stratigraphic sequence analysis using well logs suggests that incised valley fill can be identified within a nonmarine depositional setting. These gas reservoirs are composed of sandstone-rich channel-fill and splay deposits interstratified with levee and floodplain mudstones. Separate channel-fill deposits have lateral dimensions of 2,500 ft and thicknesses of 30 ft contrasted with splay deposits up to 2 mi across and up to 20 ft in thickness.

Seeligson Field Experiment. The influence of fluvial reservoir heterogeneities on the behavior of gas flow will be examined through field experiments and reservoir engineering modeling in Seeligson field. The experiment is centered on five wells in a 1 mi^2 area adjacent to two project cooperative wells (Mobil Nos. 247 and 248) drilled in 1989. Results from closely spaced geophones (30 ft) in a modification of standard VSP acquisition techniques indicate improved resolution of sandstone reservoirs compared to conventional 2-D surface seismic and VSP acquisition. An extensive cross-discipline data collection program including cross borehole tomography, near and far offset VSP's, reverse VSP's, 3-D surface seismic, cased-hole logging, borehole gravimetry, and both single and multiple well pressure testing will commence in the fourth quarter of 1990. A borehole gravity survey in one well will test the applicability of borehole gravity in old wells to determine bypassed gas distribution and porosity.

Interference testing planned for five wells will evaluate reservoirs of Zones 19-C and 15 by measuring pressure changes in observation wells caused by staggered production pulses in nearby wells. Prior to the multiple well interference testing, single-well tests will measure current reservoir pressures, near-well permeability, and completion efficiency. Information from these tests will be used to calibrate computer simulation of the interference pulse test. Reperforation and downhole equipment modifications will be required in some wells to open zone 19C reservoir sands to the wellbore and allow the installation of pressure recording equipment. Down-hole shutoff equipment is required to avoid wellbore storage effects and yield test results of sufficient sensitivity.

Current Activities in Stratton Field. During a cooperative well (Union Pacific Resources Elliff No. 40) in Stratton field, extensive core and borehole scanner measurements (Formation Microscanner, or FMS) were collected. The evaluation of methods to interpret thin beds continues, in order to find possible pay zones in thin sand bodies. A comparison of the microscanner images with core produced excellent correlation, indicating utility of FMS images for stratigraphic interpretation in non-cored zones. Wireline pressure test pressures were very useful to define depleted or partially depleted zones. Core analysis results are available from seven reservoirs in three wells and statistical analysis of core permeability versus core porosity at net overburden pressure has been used to derive a permeability index from computed log porosity. Preliminary petrophysical results have been generated for porosity, shaliness, and hydrocarbon saturation.

Preliminary findings on the computed results of twelve wells analyzed to date indicate that sand thickness, shale laminations in sand bodies, and porosity change laterally for the same zones in adjacent wells. Screening of valid wireline tester shut-in pressures within the same stratigraphic reservoirs indicate that wide variations in pressure continuity exists laterally within the same reservoir. Chronological analysis of formation pressure readings indicate wells with >70% of virgin reservoir pressure. In addition it is not uncommon for sequentially later pressure tests to have higher initial pressure than previous adjacent wells. This

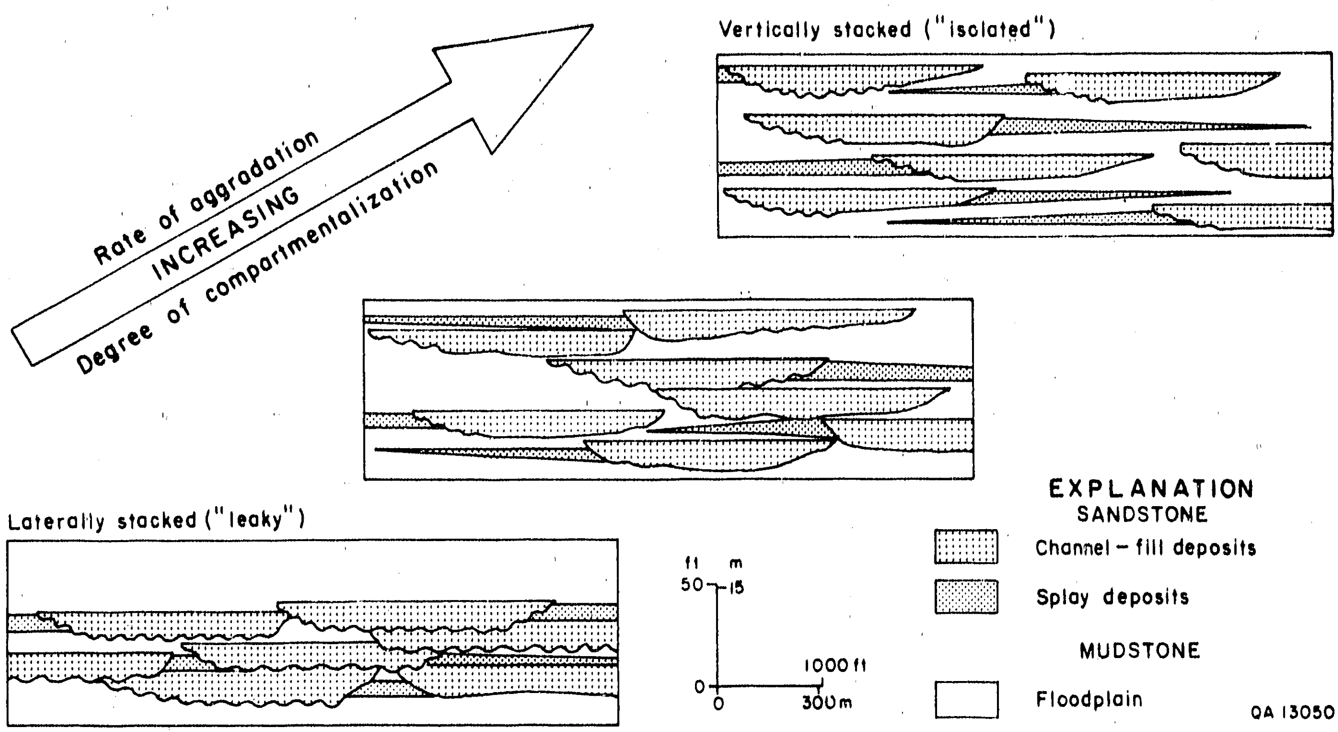

Figure 3. Schematic Diagram Illustrating Variations In Fluvial Architecture From Laterally Stacked Genetic Intervals With A Potential For Pressure Leaky Compartments To Vertically Stacked Genetic Intervals With A Potential For Pressure Isolated Compartments.

can be caused by non-uniform depletion or compartmentalization of the reservoir. Unfortunately these pressure data are not complete across all reservoirs. In future wells more shut-in pressures must be obtained to fully evaluate the impact of apparent compartmentalization on recovery and the distribution of remaining resources.

Screening Techniques For Assessment of Stratton Reservoir Heterogeneity. Public domain production data are being analyzed to identify production performance parameters which may indicate reservoir compartmentalization. In the Stratton-Agua Dulce fields, data from ~400 wells in 29 distinct reservoirs are being evaluated. The complete rate versus time decline history is being examined by an automated curve-fitting program to identify wells exhibiting evidence of pressure support interpreted as due to flow across permeability barriers. The reciprocal of initial decline rate is also being examined statistically for each reservoir as an indication of heterogeneity; this parameter is linearly proportional to the drainage volume of a well.

Detailed history matching of rate decline with a tank-like compartment model has been shown to be quite accurate for wells in several Stratton reservoirs. Production rate increase following extended curtailments is a characteristic that is represented by such models.

Engineering Techniques: Well Testing - Stratton. Single-well pressure build-up tests have been designed for five selected wells in Stratton field. These tests will incorporate a shut-in pressure build-up followed by a step-rate flow test using a high precision bottomhole gauge with surface read-out and downhole shut-off tool. These wells are in reservoirs where depositional boundaries may be detectable in the tests.

Methodology for Selecting Carbonate Study Areas. Assessment of gas reservoirs across Texas (Kosters, et. al., 1989) indicate that over 30 of the gas reserves in Texas are in Carbonate reservoirs. Regional screening results indicate that among the eight major gas plays there are 50 non-associated reservoirs with <30 Bcf. For selected west Texas and east Texas gas reservoirs P/Z data, rate-time data, and growth vintaging parameters are under consideration as field screening techniques.

FUTURE WORK

The near-term (next 2-6 months) work on the project will be directed toward three major goals: (1) completion of a report on the McAllen Ranch reservoir studies; (2) initiation and completion of the intensive data collection effort planned for Seeligson field within which multiple data types will be obtained on a coordinated basis, and (3) evaluation of compartmentalization in Stratton field that can lead to the selection of a project research well location. The latter is a project requirement in the near term and one that will allow extensive data collection that cannot be conducted in cooperative wells. Siting of this well must be coordinated with surrounding wells, either producing or abandoned in the reservoirs of interest, to conduct between-well engineering testing.

The preceeding three efforts and resulting analysis and reporting will conclude the bulk of the sandstone reservoir studies. Work will continue on Wilcox reservoirs at Lake Creek field, where coordination with another GRI project is ongoing, and where major cooperative activity with the field operator will occur in late 1990 or in 1991. Further work in the carbonate reservoir study area will lead to the first carbonate reservoir cooperative wells in 1991.

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Exploration For Deep Source Hydrocarbons in Subduction Terrain of the Pacific Northwest

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ABSTRACT

Vibroseis reflection profiles and dynamite shot records were collected in 1988, 1989, and 1990 in southern Washington from surveys across the Southern Washington Cascade Conductor (SWCC), a conductivity anomaly postulated to be associated with marine sedimentary rocks that have been carried into the subsurface by a subduction zone active in the Eocene.

Approximately 238 km of seismic survey lines were collected traversing the SWCC in an east-to-west direction, and with one survey extending north in the interior of the anomaly. Surveys were done to assess the petroleum potential and possible deep source origins of the petroleum that could be related to the subduction of the accretionary prism sediments. If the thick sequences of marine shales are present, they could be source beds for the migration and entrapment of hydrocarbons into the abundant, known structures traversed by these seismic surveys. Seismic data collected have revealed much about the subsurface structure and have imaged complex structural features below 10 km that cannot be completely resolved and that have critical importance to evaluating the occurrence of the deep marine section.

This report relates the results of exploration in the area and provides interpretations for the seismic sections in an effort to define the area's petroleum potential. Major structural features, such as the Morton and Skate Creek anticlines, could act as hydrocarbon traps; however, adequate source and reservoir rocks are undefined.

Further seismic surveys were carried out in the summer of 1990 in an attempt to define the subducting layer and its associated sediments. Additional geologic mapping and well analyses were also accomplished to evaluate the complex subsurface geology. These data have yet to be processed, and the integrated assessment of the petroleum potential for the region must await the new seismic section's processing and interpretation, which is expected to be completed by mid-year 1991.

Objective

To determine the natural gas potential of sediments associated with plate tectonic subduction zones and pull-apart basins in the Pacific Northwest.

PLATE TECTONICS AND SUBDUCTION OF SEDIMENTARY ROCKS

Plate tectonics movements of the Earth create basins wherein relatively rapid sedimentation can occur. Abundant organic material can accumulate at these sites to be later transported to depths within the Earth's crust, where increased pressure and temperature provide conditions conducive to the conversion of organic material to hydrocarbons.

Such is believed to be the case in the Pacific Northwest and, in particular, southwestern Washington (Figure 1), where recent studies have delineated a present subduction zone involving the Juan de Fuca plate underthrusting the North American plate (Figure 2).

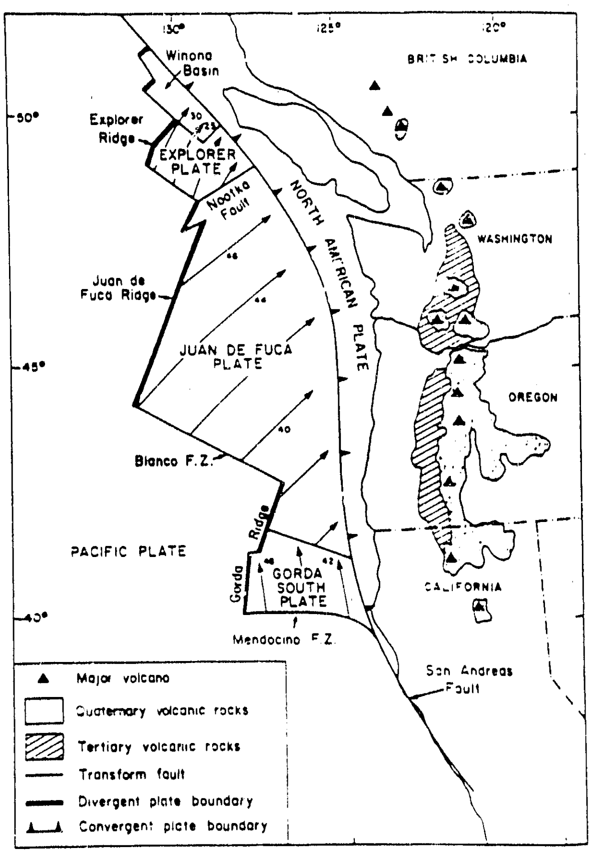

Figure 1. Plate-Tectonic Map of the Coast of the Northwestern American Continent Showing Major Crustal Boundaries. Arrows indicate the directions of net convergence in millimeters per year. Figure from McBirney (1978) and Riddehough (1984).

The oceanic layer, with its overlying sediment and captured sediment from the accretionary prism at the frontal lobe of the North American Plate, underthrusts the continental mass and then, at an increasing angle, is subducted into the lower continental crust and upper mantle. Sediments may be carried to greater depth by the conveyor-belt action of this subducting layer. Marine and terrestrial materials deposited in previously formed basins are carried to depths appropriate to convert the organic material to hydrocarbons. Hydrocarbons may then follow pathways along existing faults and fractures and migrate to entrapment structures at economic drilling depths in these terrains.

The creation and migration of subduction zones may be episodic. In geologic time, different geographically located subduction zones, with their captured and altered sediments, may exist in the subsurface as indicated in Figure 2. Such is postulated to be the case in southwestern Washington, where the United States Geological Survey (USGS) magnetotelluric surveys have detected an anomalous conductivity zone thought to be related to deep crustal marine sediments that were carried to depth by the conveyor-like action of the subducting oceanic layer.

Several magnetotelluric surveys have defined the anomalous conductivity zone between Mt. Rainier, Mt. St. Helens, and Mt. Adams (Figure 3). The magnetotelluric (MT) method is a way of determining the electrical conductivity distribution of the subsurface from measurements of natural

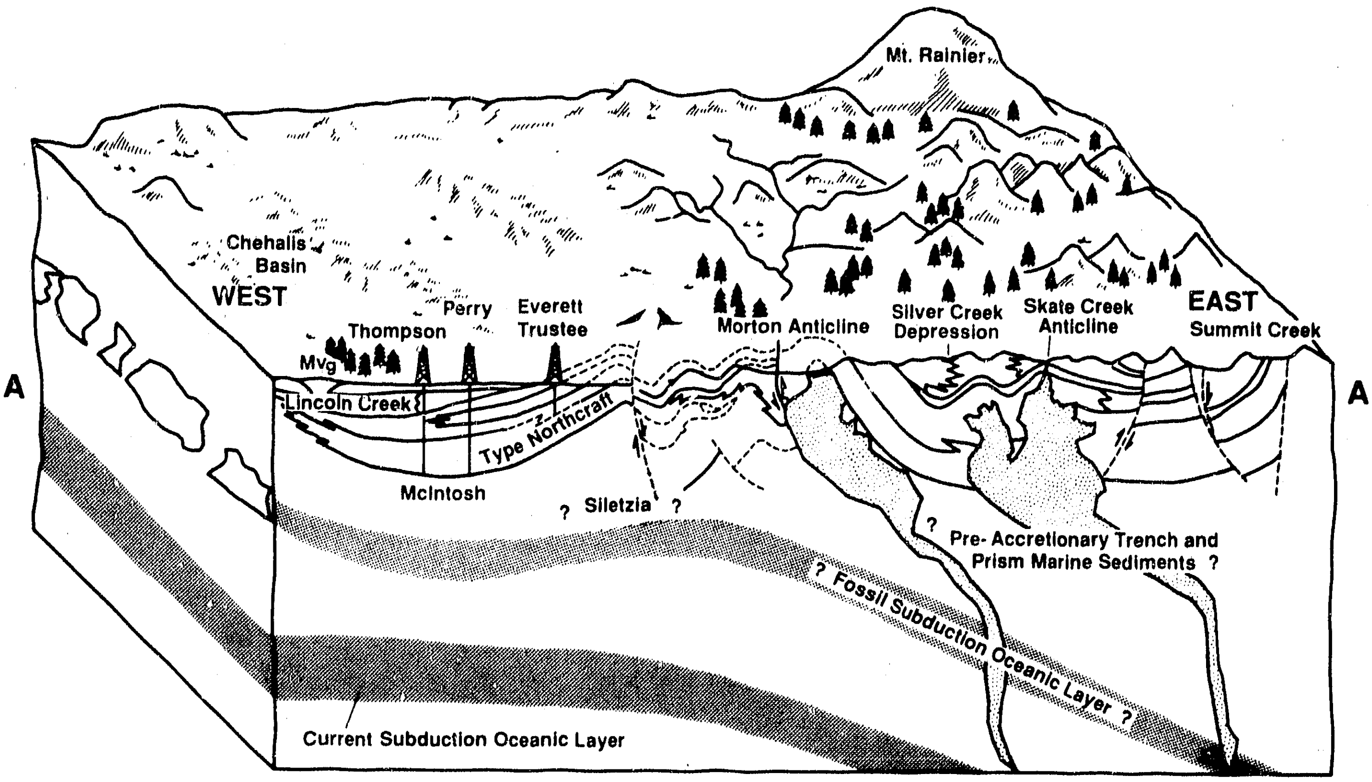

Figure 2. Tectonic Framework of Southwestern Washington Showing Postulated Subduction Zones and Accreted Sediments
(Modified after Phillips and Walsh 1989)

transient electric and magnetic fields on the surface of the Earth. Measurements are absolute, so their interpretation gives true resistivity/conductivity values and true depths -- not just anomalies. The maximum depth of penetration depends on how deep the low frequency electric and magnetics fields penetrate. Modeling of resistivity versus depth is done with a trade-off between thickness and resistivity in MT modeling. Depths to the tops of conductive bodies are better determined than depths to tops of resistive layers. Model cross-sections defining one- and two-dimensional interpretations of the subsurface have been constructed (Stanley and others 1987), outlining the anomalous conductivity zone in the subsurface (Figure 4).

Units of resistivity less than 5 ohm-m define a conductivity package, the Southern Washington Cascade Conductor (SWCC), at depths of only 1 to 3 km near the axis of the Morton anticline (Stanley and others 1989). Near-surface rock resistivities are 30 to 500 ohm-m and are interpreted to represent volcanic formations, similar to many of those exposed at the surface, and to also contain some continental sedimentary rocks. Rock units to the west with resistivities of 150 ohm-m correspond to magnetic and gravity highs and have been interpreted as volcanic seamount rocks and oceanic crust. These rocks were "rafted in" during plate movement and subduction, and subsequently

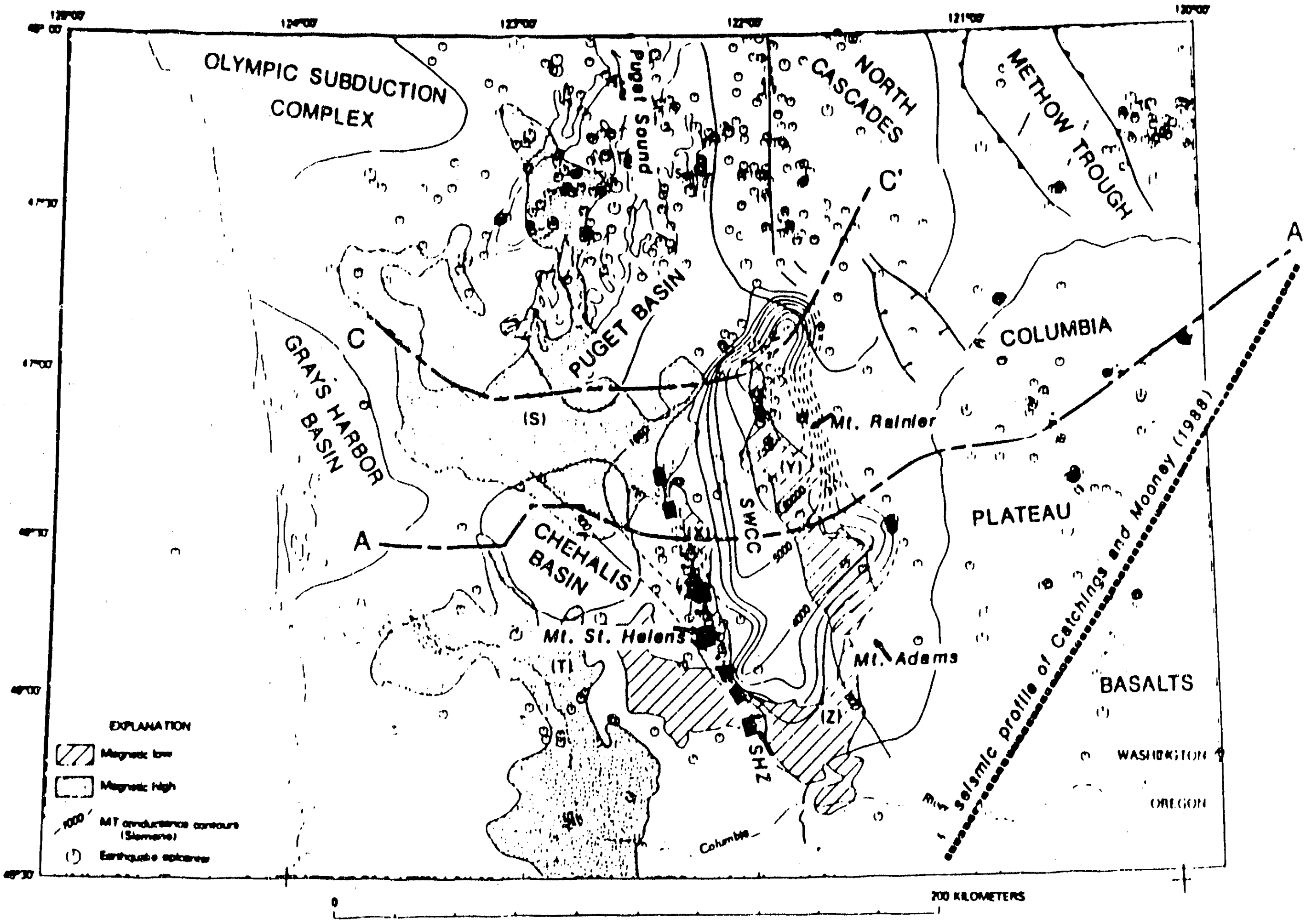

Figure 3. Map of Southwestern Washington Showing Magnetotelluric Surveys and the Southern Washington Cascade Conductor (SWCC) (After Stanley and others 1989)

caused the blockage that moved the subduction zone to the west (the present-day subduction zone), leaving the "fossil" subduction zone and the associated hydrocarbon generating sedimentary rocks at the SWCC.

REGIONAL GRAVITY, MAGNETICS AND SEISMICS AND THEIR RELATION TO GEOLOGY

The southwestern Washington Cascades include three Quaternary volcanoes of the magmatic arc associated with the North American-Juan de Fuca convergent margins: Mt. St. Helens, active since the May 1980 eruptions; Mt. Rainier, the largest Cascade volcano; and Mt. Adams, corresponding in size to the pre-eruptive Mt. St. Helens. Much of the region near the three volcanoes is covered by volcanic flows, making geologic mapping and geophysical surveying of the subsurface very difficult. East of the Cascade Range are the extensive Columbia Plateau basalts. To the west are the sedimentary rocks and basalts (volcanic flows) of Tertiary age, which include the Crescent Formation and Siletz River basalts that are

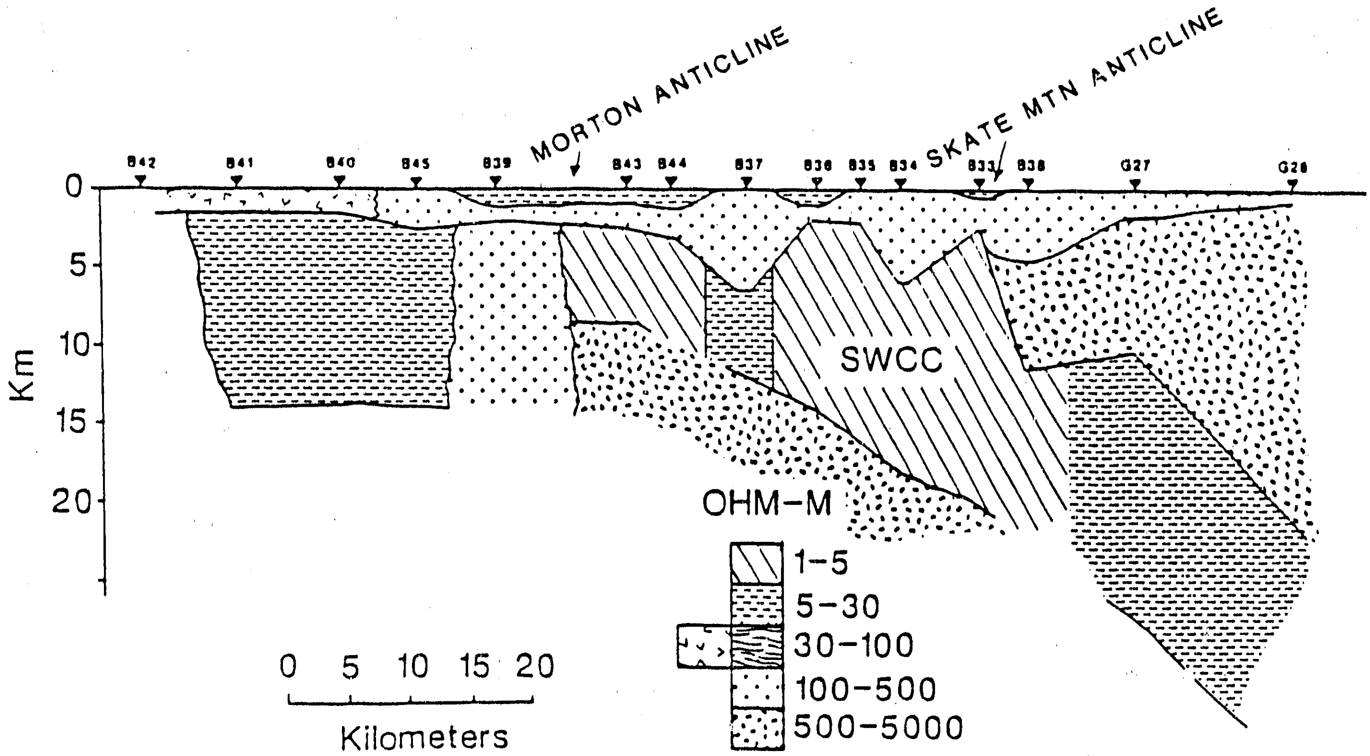

Figure 4. Cross-Section of the Southern Washington Cascade Conductor (SWCC) (After Stanley and others 1989)

believed to be part of an accreted seamount complex (Duncan 1982).

Regional magnetic, gravity, and seismic studies provide details of the offshore Cascadia Basin with an interpreted 500 m of marine sediments overlying 5 km of marine basalts, with the Moho occurring about 10 km below these basalts (Finn 1988). The continental shelf and slope consist of as much as 13 km of marine and continental sediments. The present subduction zone, interpreted with the aid of seismic refraction, earthquake hypocenter, and teleseismic P-wave delay data, dips at about 0.6° under the Cascadia Basin, increasing to 9° about 110 km offshore and continues at this dip to just before the longitude of Puget Sound. Under the North American plate, the Juan de Fuca plate, on an east-west profile, has an effective southeast dip of about 11° to 20° -- the increase to 20° to 25° occurs at about the longitude of central Puget Sound. The dip of the Juan de Fuca plate east of the longitude of Puget Sound is constrained by teleseismic P-wave residuals, which indicate the plate is dipping greater than 45°. The 45° dipping section of the Juan de Fuca plate reaches a depth of about 100 km under the Goat Rocks Volcano, which is about the depth of most plates over which magmatic arcs usually occur (Dickinson 1970). Figure 5 illustrates the geometry of the present subduction section in southwestern Washington and is shown to put in perspective the relative measurements (and depths to major discontinuities) of a subduction zone (Finn 1988). Accordingly, one would expect comparable geometries and depths to be features of "fossil"

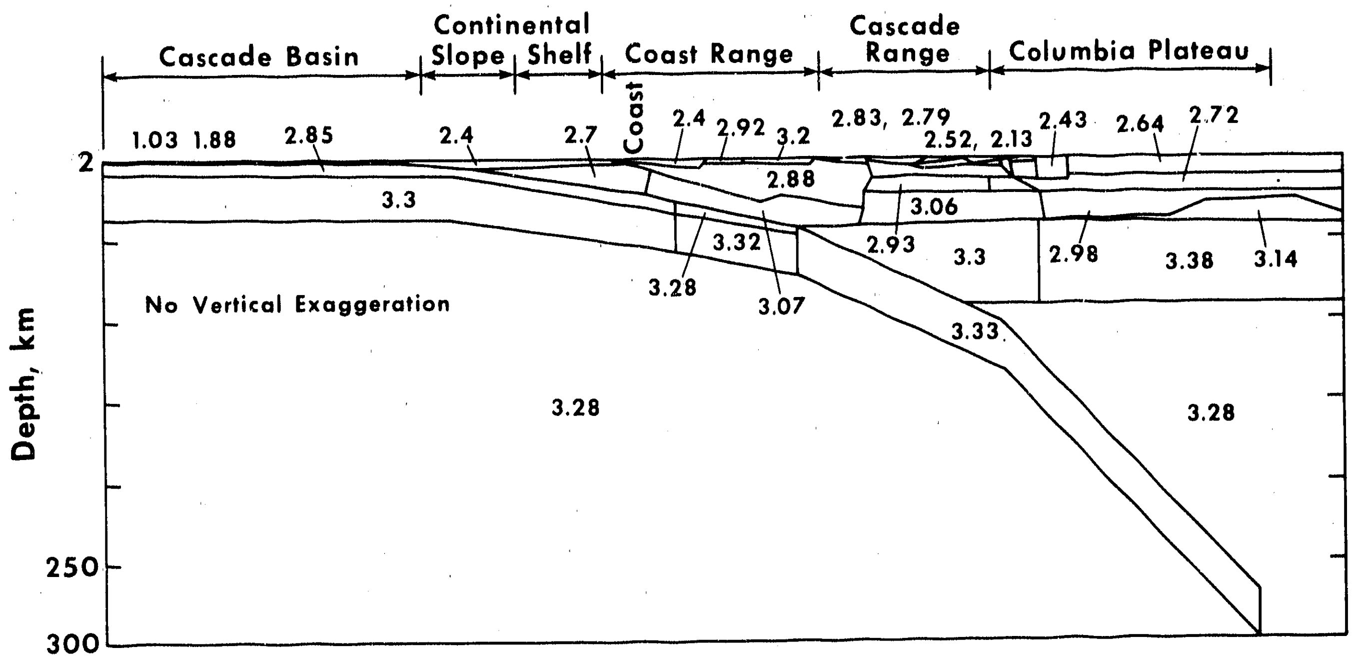

Figure 5. Cross-Section of Present Subduction Zone in Southwestern Washington With Density Values for Lithologies (Finn 1988)

subduction zones, unless considerable uplift has occurred that raised comparable features to shallower depths in the Earth's crust.

Gravity surveys, which measure slight variations in the gravity field of the Earth caused by differences in surface and subsurface rock densities, define a relatively flat field in offshore Washington. This field shows a low association with the sediment-filled trench of the oceanic crust as it subducts. High measurements onshore are associated with the Coast Range oceanic terranes that were accreted to the continent. The major high topographic areas, such as the Cascade Range, have associated gravity lows, probably reflecting rocks that provide isostatic compensation for the mountains.

Aeromagnetic surveys measure slight variations in the magnetic field of the Earth that are caused by differences in the magnetization of rocks at and below the surface and are more sensitive to shallow sources than gravity. Offshore Washington shows magnetic stripes associated with reversed and normal portions of the seafloor. As the Juan de Fuca plate begins subduction beneath the slope and shelf, the anomalies disappear and a magnetic quiet zone occurs, caused by nonmagnetic sediments overlying the oceanic crust. Magnetic highs are associated with the exposed section of Crescent basalt in the onshore Coast Range that extends partially over the Puget lowland, which is mostly covered with surface volcanic rocks (Finn 1988). Magnetic highs in southwest Washington are also caused by (1) the magnetic terrane of Mt. St. Helens and Mt. Adams, (2) intrusives such as that underlying Goat Rocks Volcano, and (3) andesite and basalt flows. A magnetic low surrounds highs of the volcanoes and appears associated with anticlinal structures (e.g., Morton and Skate Creek anticlines) that thin the surficial magnetic volcanic rocks and bring sediments within 1 km of the surface (Finn 1988).

The interpretation of marine sedimentary rocks deeply buried in southwest Washington, proposed by Stanley and based on a MT conductivity anomaly, has been found to be compatible with aeromagnetic and gravity surveys in the area. The magnetic low that surrounds and interrupts the highs associated with the volcanoes and volcanic rocks within the triangle formed by the three volcanoes is not associated with surface rocks, but approximately encloses the conductivity anomaly. A gravity low follows the northwest side of the circular magnetic low of the SWCC, but the low does not correlate with the south and east sides of the magnetic low of the SWCC (Finn 1988).

STRESS CONDITION IN SOUTHWESTERN WASHINGTON

The definition of the stress regime in southwestern Washington has been aided by the seismic network installed after the Mt. St. Helens eruption of 1980. That network has located events that have outlined a well-defined northwest trending belt of seismicity named the St. Helens Seismic Zone (SHZ) in which most of the earthquakes occur in the upper 5 to 10 km of the crust (Figure 6). However, no surface expression of any strike-slip faults occurs at the surface.

Seismicity data from the Mt. St. Helens network show that the SHZ coincides approximately with the western boundary of the SWCC, which also coincides with a magnetic low (Finn 1988). The strike-slip zone active in the SHZ may be located at the western margin of the SWCC, where a postulated accretionary contact allows the slip component of oblique subduction to be accommodated (Stanley and others 1989). Strike-slip faulting in the southern Washington Cascades lies at the southern end of a belt of right-handed slip related to oblique convergence of the Juan de Fuca plate and its predecessors. From 400 to 1,000 km of strike slip have been postulated for the borderland terranes of British Columbia and Alaska in post-Mesozoic time.

Paleostratigraphy and structure prior to the Eocene for Washington Coast Range basalts are poorly known. Paleoreconstruction of possible basin settings could be complicated by the 100 to 200 km of right-hand displaceme ıt postulated to have occurred since the Mesozoic in the region south of the Straight Creek Fault, a major structural feature north of the SWCC. If this amount of strike slip has occurred since the accumulation of sediments in the SWCC, the original deposition location would be in Oregon near the Blue Mountains, where Mesozoic forearc sediments have been mapped.

Rotation of the Coast Range from paleomagnetic evidence indicates a relative clockwise rotation with respect to the North American plate of about 25° in the north and up to 75° in the south. The effect of rotation in the southern Washington Cascades may not be important, because the paleomagnetic data show the pole of rotation to be close to the surveyed area of the SWCC (Stanley and others 1989). Much of the stress evidence that might be disclosed by fault studies is covered in this volcanic terrane. Active strike slip apparently occurs in the area of Mt. St. Helens where Weaver and Smith (1983) have mapped the right-lateral slip zone by active seismicity -- the SHZ.

Differential slip along such proposed fault zones has created Tertiary pull-apart structures that have been subsequently filled with thicknesses of continental sediments;

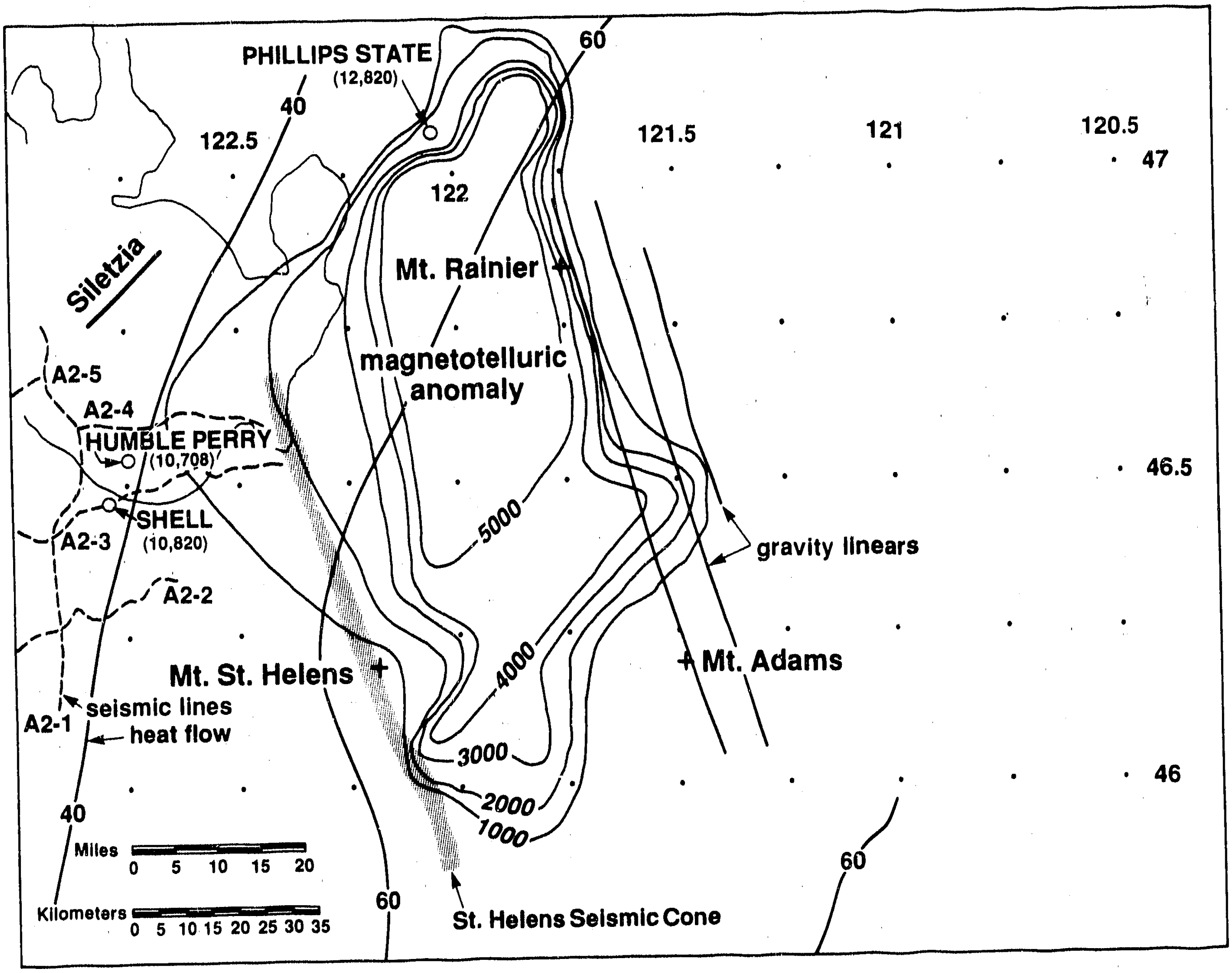

Figure 6. Geophysical Survey Results for Southwestern Washington Delineating the St. Helens Seismic Zone (SHZ)

these continental sediments have been postulated for the eastern Puget Sound, the Cascades axis, and the eastern Cascades flank by Johnson (1985) and Evans and Johnson (1989). A major transcurrent strike-slip fault continuing from the San Juan Islands north of Seattle and through the Puget lowland has been postulated to explain some of the rifted basins. However, no continuous direct evidence exists for such a fault (Johnson 1984).

GEOLOGIC SECTION OF SOUTHWESTERN WASHINGTON

Geologists of the Washington State Department of Natural Resources are responsible for the geologic mapping of the state, and in the course of mapping, construct geologic sections to aid in subsurface interpretation. Figure 7 is a constructed geologic section from the Washington

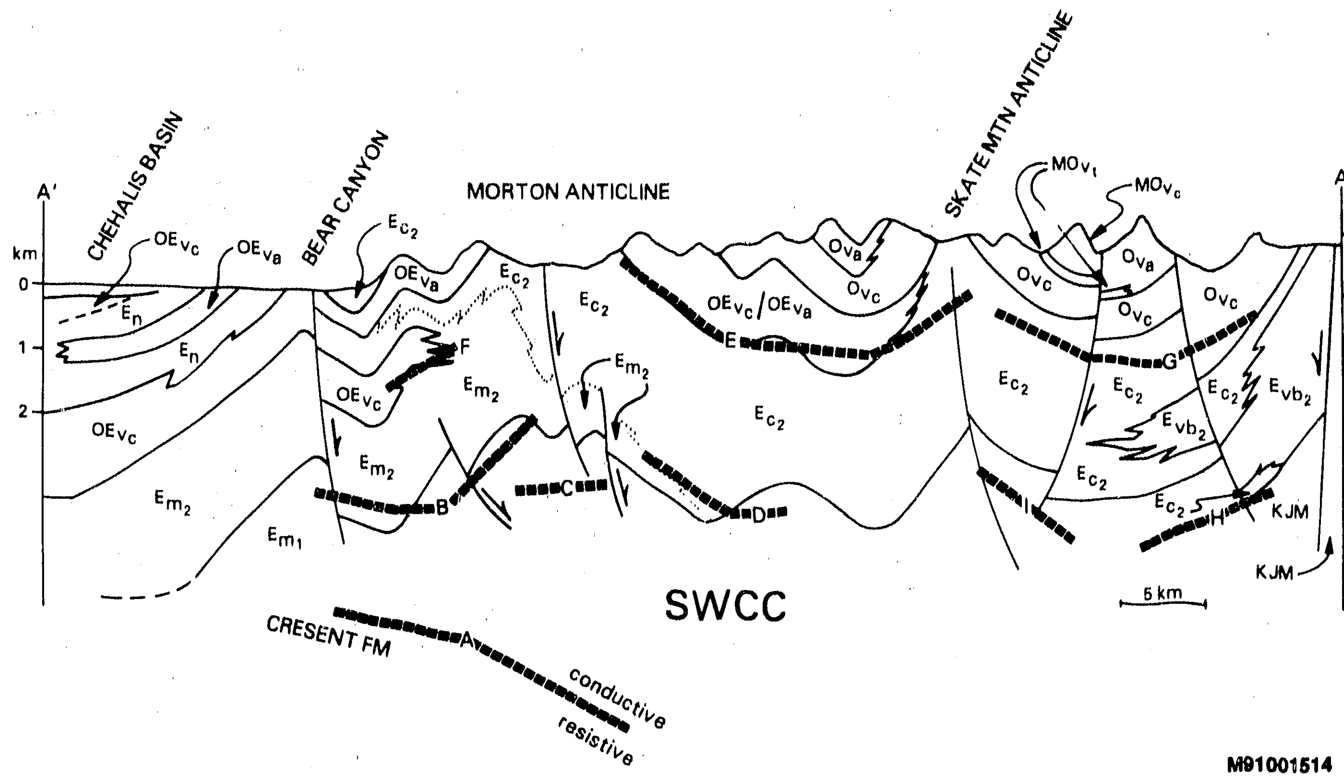

Figure 7. Southwestern Washington Geologic Section From Washington State Geologic Survey, Mapping From the Chehalis Basin to the Cascade Range (Stanley and others 1989, and Phillips and Walsh 1989)

offshore near Gray's Harbor that passes eastward through the survey area of interest and terminates at the Tieton Inlier east of the Cascade Range. This section displays the interpreted basin development from west to east across the southwestern section of Washington and is developed from various sources including geologic and geophysical data, surface geologic mapping, well logs, and seismic, gravity and magnetic surveys. The section shows the surface geologic influence in that the upper crustal section is made up of a series of basins and does not reflect a subduction influence on near-surface geology or in basin development (Lingley 1989, and Phillips and Walsh 1989).

ORGANIC CONTENT OF SEDIMENTS AND ESTIMATES OF MATURATION

The McIntosh Formation and older marine shale units make up the deeper part of the Chehalis Basin and probably the deeper portions of the basins to the east. The McIntosh Formation outcrops at Bear Canyon, and the probable time equivalent Carbonado Formation exists at the surface in the eroded axis of the Morton anticline; however, both have limited organic content. In fact, the value for the total organic carbon in Cenozoic marine sedimentary rocks in southwest Washington, as indicated from

100 samples, is about 1% (Armentrout and Suek 1985). Some intervals in wells drilled in the area show averages near 2%. Paraffin oil from 7,060 to 7,120 ft in the Phillips well drilled northwest of Mt. Rainier is interpreted to have migrated from greater depths (Stanley and others 1989).

Time-temperature reconstruction for the Mist gas field in Oregon indicates the rocks of the Cowlitz Formation, which is a time equivalent to the McIntosh, were in the oil generation window 33 million years ago, a window which corresponds to burial depths of approximately 5 km and temperatures to 130°F. Accordingly, sediments of interest for generation of hydrocarbons must have been near these depths.

In general, rocks sampled in Washington and northwestern Oregon represent low maturity, which makes the area of less interest to explorationists. The proximity to heat sources, such as those associated with volcanic massifs and the projected depths to the postulated deep accretionary sediments, should imply greater maturity and, perhaps, overmature organics at depth.

THE POTENTIAL FOR FINDING ADEQUATE RESERVOIR ROCKS

A potential reservoir rock in the survey area is the McIntosh Formation, the time equivalent to the Cowlitz Formation sandstones, which are the natural gas-producing rocks in the Mist gas field. Cowlitz sandstones are exceptional in that most Tertiary sedimentary rocks of western Washington and Oregon have low porosity owing to their volcaniclastic origin and subsequent digenesis. The porosity and permeability of possible reservoir rocks are expected to decrease as the Cascade Range is approached and the amount of volcaniclastic rocks increase (Lingley 1989).

Several questions remain concerning source rocks, their organic content and maturity, and the occurrence and location of appropriate reservoir rocks. High resolution surveys might be used, not only for defining structures of interest, but also for correlating formations from control points in the Chehalis Basin and for defining lithologies and their physical properties. Accordingly, deep high resolution seismic surveys were initiated in the summer field season in 1988 in an attempt to find answers to these questions. Prior to initiating these surveys, however, available commercial seismic survey data were purchased and interpreted to gain knowledge of the subsurface in the area of interest and to provide information about the effectiveness of such surveys in this difficult volcanic terrane.

COMMERCIAL SEISMIC SURVEYS AND WELLS IN THE CHEHALIS BASIN

Seismic reflection surveys are the principal geophysical method employed in oil and gas exploration because they provide the best resolution of subsurface features. When combined with well logs and synthetic seismograms created from sonic well logs, they provide the necessary control for correlating known formations and their properties from the well to the outlying subsurface section.

The StrataSearch commercial seismic survey line through the Chehalis Basin was purchased and interpreted in association with synthetic seismograms from several wells drilled in the basin, which provided control for extending formation correlations (Boswell and others 1989). The survey line is shown in Figure 8, and the seismic section with some of the well synthetic seismograms

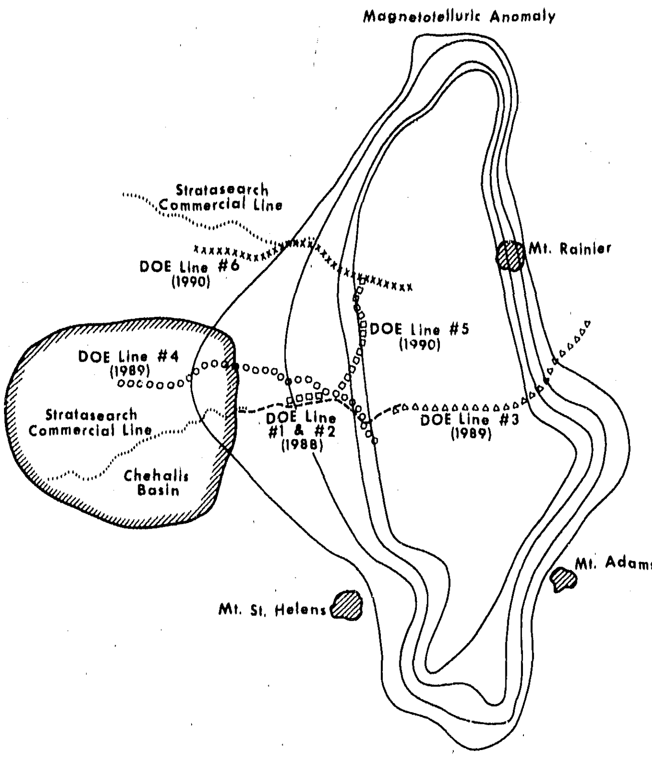

Figure 8. Seismic Survey Line Map for Seismic Surveys in Southwestern Washington

used for correlation control is shown in Figure 9. The Shell Thompson No. 1 well in the Chehalis Basin was drilled to 10,820 ft and penetrated about 7,300 ft of coal-bearing, marginal marine sediments of the Eocene Skookumchuck Formation, some 3,500 ft of the Northcraft volcanic rocks, and apparently penetrated the McIntosh Formation that outcrops just east of the basin at Bear Canyon. A small oil seep has been discovered in the McIntosh at Bear Canyon (Hedges 1949), and surface rock samples containing carbonaceous material found here give vitrinite reflections of 0.5%. Additional wells have been drilled in the Chehalis, none of which found commercial hydrocarbons.

The StrataSearch seismic line's west end starts at the outcrop of the Crescent ridge basalts, and the basin well logs provide good velocity control, allowing identification of formations down to about 10,000 ft.

At the deepest point of the line, there appears to be about 11,000 ft of sediments beneath the Northcraft volcanics, and perhaps 5,000 ft is the McIntosh Formation, which is known at the surface and subsurface at Bear Canyon to the east and correlates with its time equivalent at the exposed center of the Morton anticline (Carbonado Fm.). These sediments may have petroleum potential as indicated from some gas shows in wells and by the fact that the McIntosh is correlatable with the Cowlitz Formation, which is the gas-producing horizon in the Mist Field in Oregon, some 100 km south and east of the SWCC. The Mist Field has good reservoir sands interpreted to be a special part of the fore-arc complex. The hydrocarbon source for the gas has not been discovered, but is thought to be from depocenters to the east or west (Armentrout and others 1985).

The StrataSearch Line shows textbook basinal development with the McIntosh and deeper formations lying as quasi-concentric deposits above the basement. The McIntosh shallows to the east and thins over the structural sill where it outcrops at Bear Canyon. It is then interpreted to infill the deeper section of the basin that occurs to the east in which the Morton anticline is found that exposes the time equivalent to the McIntosh, the Carbonado Formation, at its core. The potential for continuing a series of basins to the east in which formations found in the Chehalis Basin make up the series of layers presents a possible alternative theory to having subduction layers near the surface in southwestern Washington.

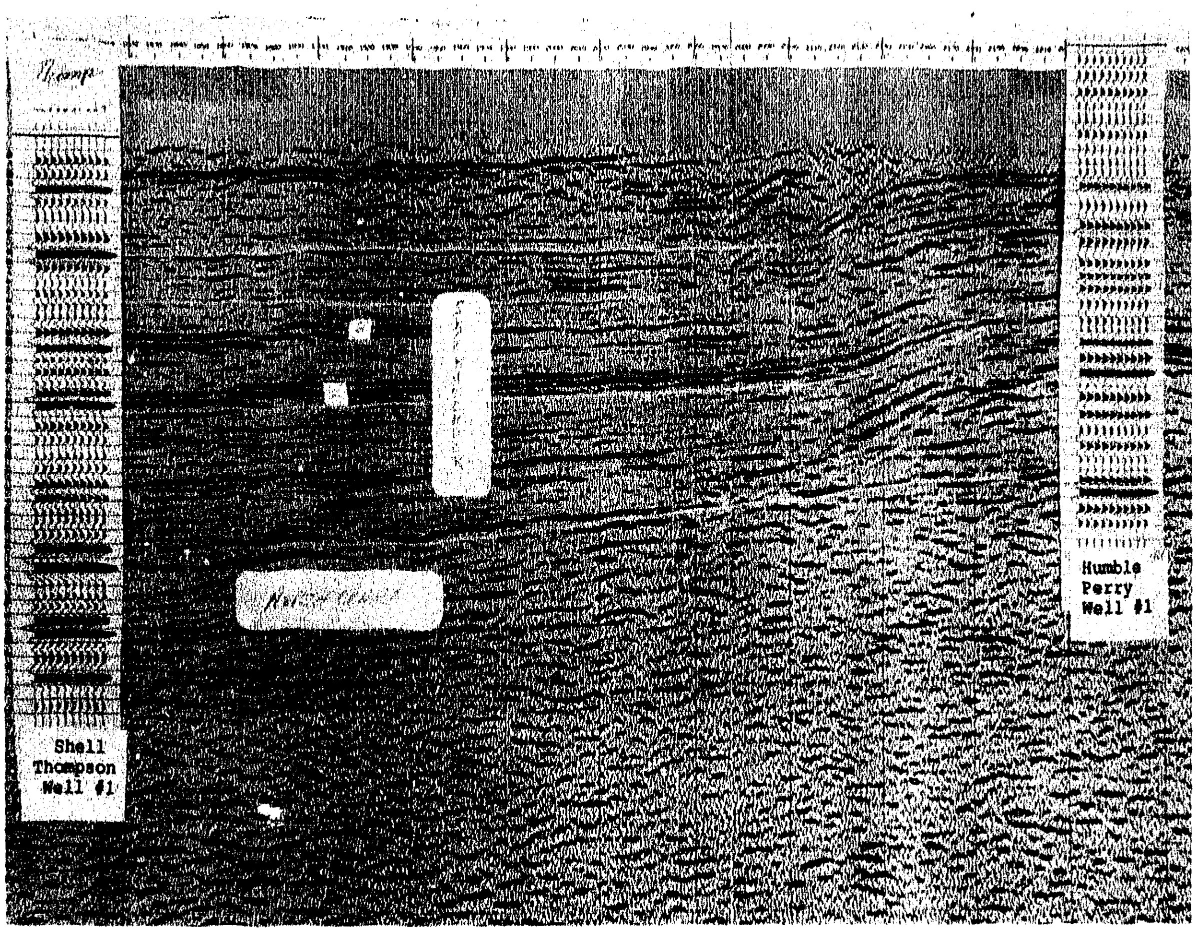

Figure 9. StrataSearch Seismic Section for the Eastern Chehalis Basin With Well Synthetic Seismogram Control

DOE/GEOSYSTEMS, INC. SEISMIC SURVEYS, 1988

The seismic survey of 1988 was done over the western gradient portion of the SWCC, shown on Figure 8, in an effort to image the proposed subducting layer and define the structure of the postulated subducted sediments. The surface array varied in length from 10 to 30 km and used an energy source of five vibrators in tandem, which downswept source energy frequencies from 39 to 8 Hz.

Survey parameters are outlined in Table 1. Lines 1 and 2 were run along State Highway 12 and covered not only the SWCC western gradient, but also the western limb of the Morton anticline. Line 1 was surveyed with detector group intervals of 30 m. Line 2, which extended the survey to within 0.75 km of Randle, Washington, had group intervals decreased to 20 m to improve resolution (Figure 8). The postulated subduction layer has been interpreted as the bottom-most layer imaged in the seismic section of Line 1 shown in Figure 10. It is seen down to about 2.8 seconds two-way travel time where it becomes indistinct, but definitely appears to underlie the bottom-most layer to the east, with which it might otherwise be correlated.

Table 1. Survey Parameters for the DOE/GeoSystems, Inc. Seismic Surveys

Seismic Crew GeoSystems, Inc.	
Source	5 Vibrators
Sweep	9-39 H3 Varisweep Downsweep
Sweep Duration(s)	15
Total Recording Time(s)	30
Correlated Record Length(s)	15
Sample Interval(m/s)	4
Spread Geometry	Offend
Geophones/Group	6
Group Interval(m)	20
No. of Channels	1024
Coverage	128 to 171 - Fold

In Line 2, the layer is not imaged. When both seismic survey segments are processed and joined together, the postulated top of the subduction layer is less visible.

Beam steering, a process in which energy from reflectors at specific azimuths and inclinations is enhanced, was used to obtain the image of the more prominent bottom-most layer in Line 1 (Figure 11), herein interpreted as a possible subduction zone upper layer. In Figure 12, the beam-steered result is interpreted as a possible rifted basin, viewing the continuance of the dipping layer that continues to the two-way travel time of 4.0 seconds, as an artifact of the beam-steer process and possible diffraction effects.

Questions remain concerning the interpretation of the bottom-most layer as the upper layer of the subduction zone and, therefore, of its being a pointer for the associated accretionary sediments at depth. The alternative hypothesis is that it could be the bottom-most imaged layer of a rifted basin in which that layer has been displaced along the obvious faulting that has disrupted the western limb of this basin, and the apparent extension of the layer may be caused by processing and/or its extension as a result of diffraction of seismic waves. As noted when both surveys are processed together, the lower-most layer is less inclined to be interpreted as a continuous subducting layer, but the obvious extensive faulting prevails. It is noteworthy that the extension of the SHZ of seismicity is related to what is believed to be a major fracture zone passing through this faulted and fractured system. The two lines reveal the Morton anticline and its 2 to 3 km of relief, suggesting the possibility of having a significant entrapment structure for hydrocarbons and an attractive exploration target if appropriate reservoir rocks exist.

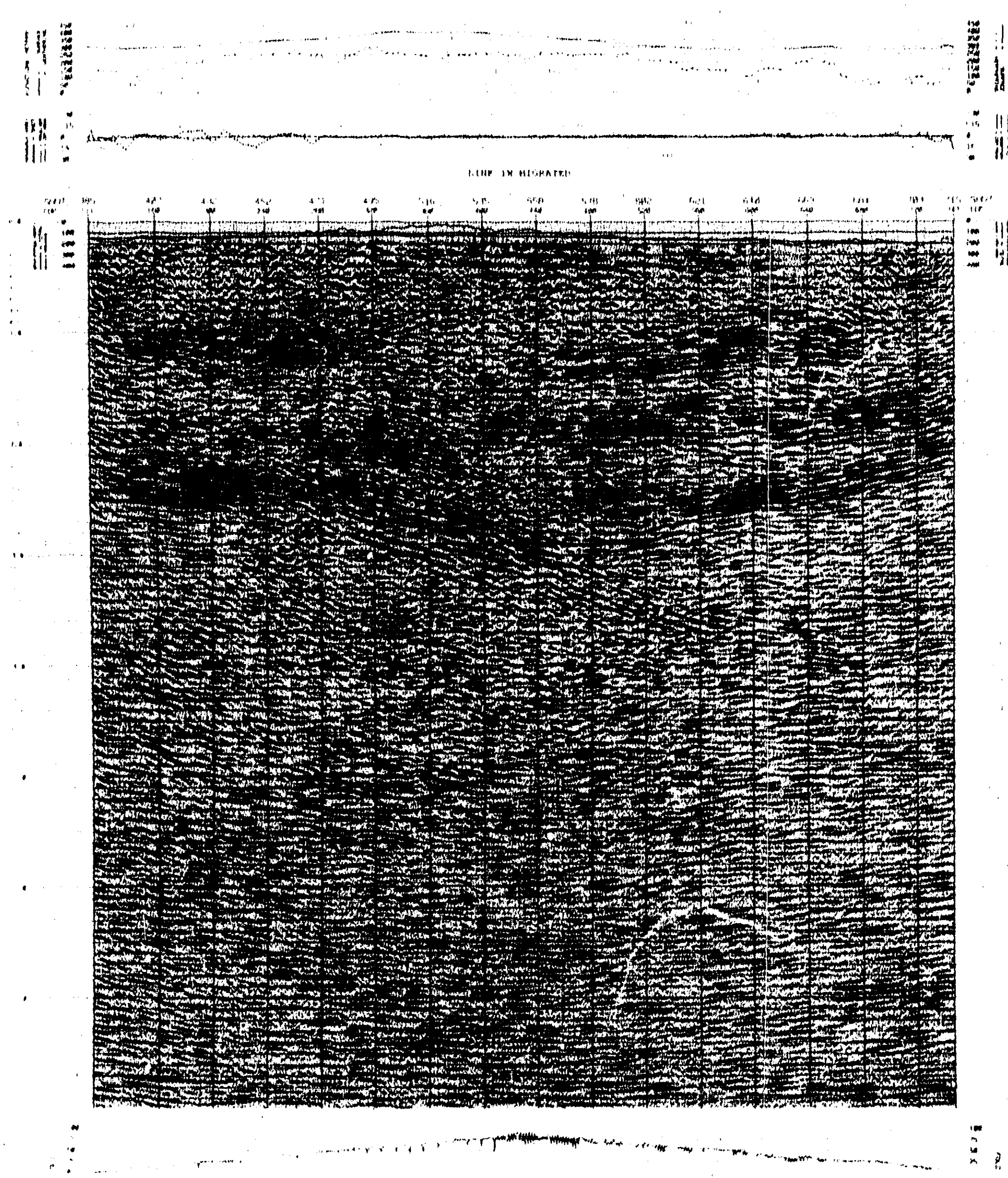

Figure 10. Seismic Section for Line 1 Showing the Deep Eastward-Dipping Layer

DOE/GEOSYSTEMS INC. SEISMIC SURVEY LINE 3

Survey Line 3 extended Lines 1 and 2 to the east beyond Randle, Washington, along Highway 12 through the Cascade foothills, crossing over the eastern gradient of the SWCC and terminating east of Packwood, Washington, as shown in Figure 8. The processed and migrated seismic section shown in Figure 13 displays the Skate Creek anticline with relief comparable to that of the

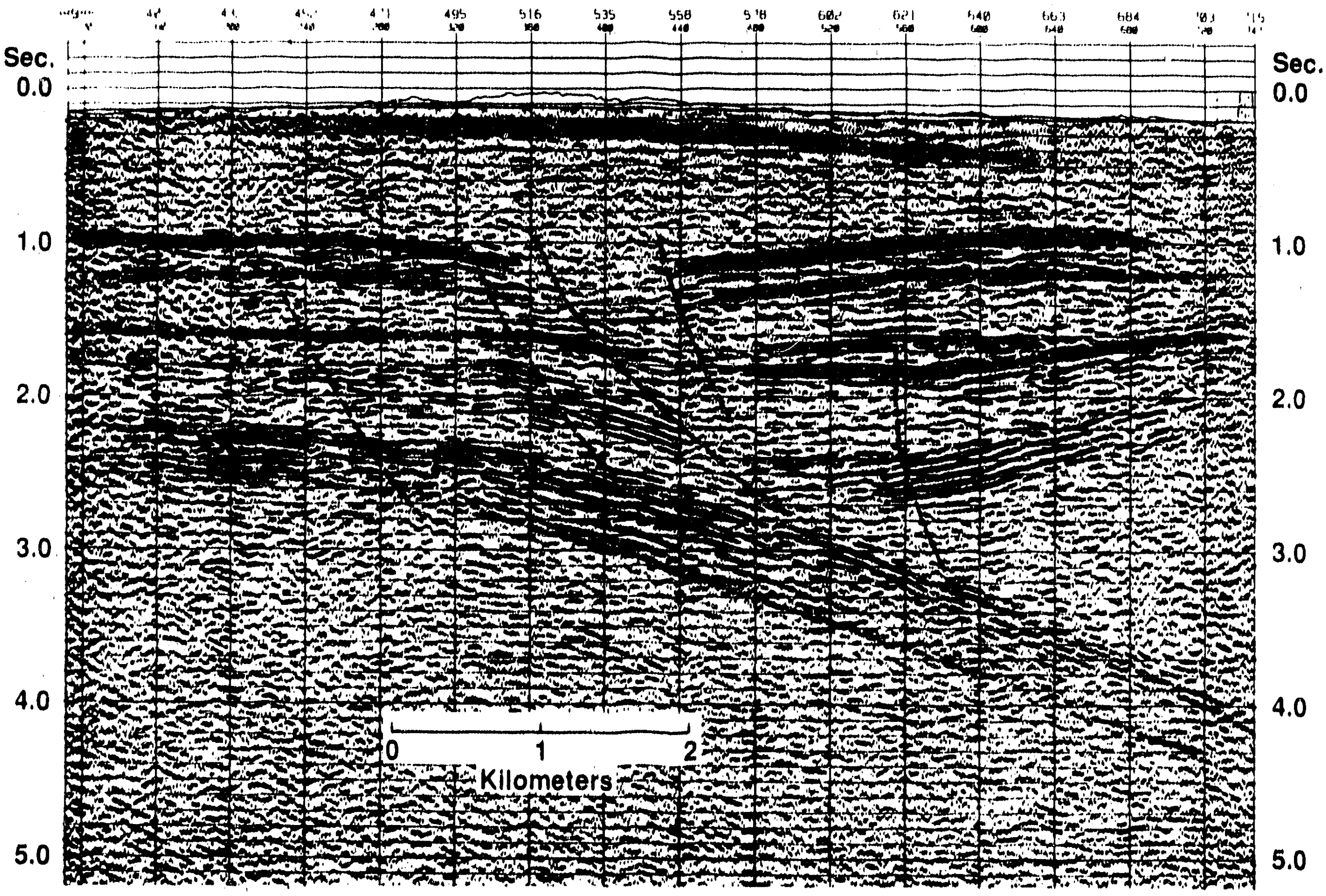

Figure 11. Straight-Line Correction and Beam-Steered Seismic Section of Line 1 Interpreted as a Subduction Zone

Morton anticline, and its location considered to be over the highest thermal activity where Oligocene volcanic centers, Miocene intrusives, and the present magmatic arc are centered (Stanley and others 1989). The eastern end of the survey shows west-dipping layers underlying the Cascade Range. These structural dips are also seen in the surface volcanoclastic layers. The deep section imaged here may be rocks comparable to the Mesozoic complex of the Tieton Inlier, which includes the Russell Ranch Group of rocks exposed immediately east of the Cascade Range.

DOE/GEOSYSTEMS INC. SEISMIC SURVEY LINE 4

Survey Line 4, initiated at the east end of Riffe Lake, passed westward back over the Morton anticline along a section of Highway 12, through the town of Morton, and then followed Highway 508 past the Bear Canyon exposure of the McIntosh Formation and continuing through the Chehalis Basin along a route subparallel to Lines 1 and 2, but displaced some 7 km to the north. Line 4 terminated approximately 1 km east of Interstate Highway 5. The seismic line was run to obtain a different survey angle on the postulated subduction zone and the Morton anticline and to tie seismic interpretation to the McIntosh Formation exposure in Bear Canyon. The survey also provides a different imaged section of the Chehalis Basin, which can be compared to the purchased commercial line. Figure 8 shows the survey line relation to the geographic features of the area. Figure 14

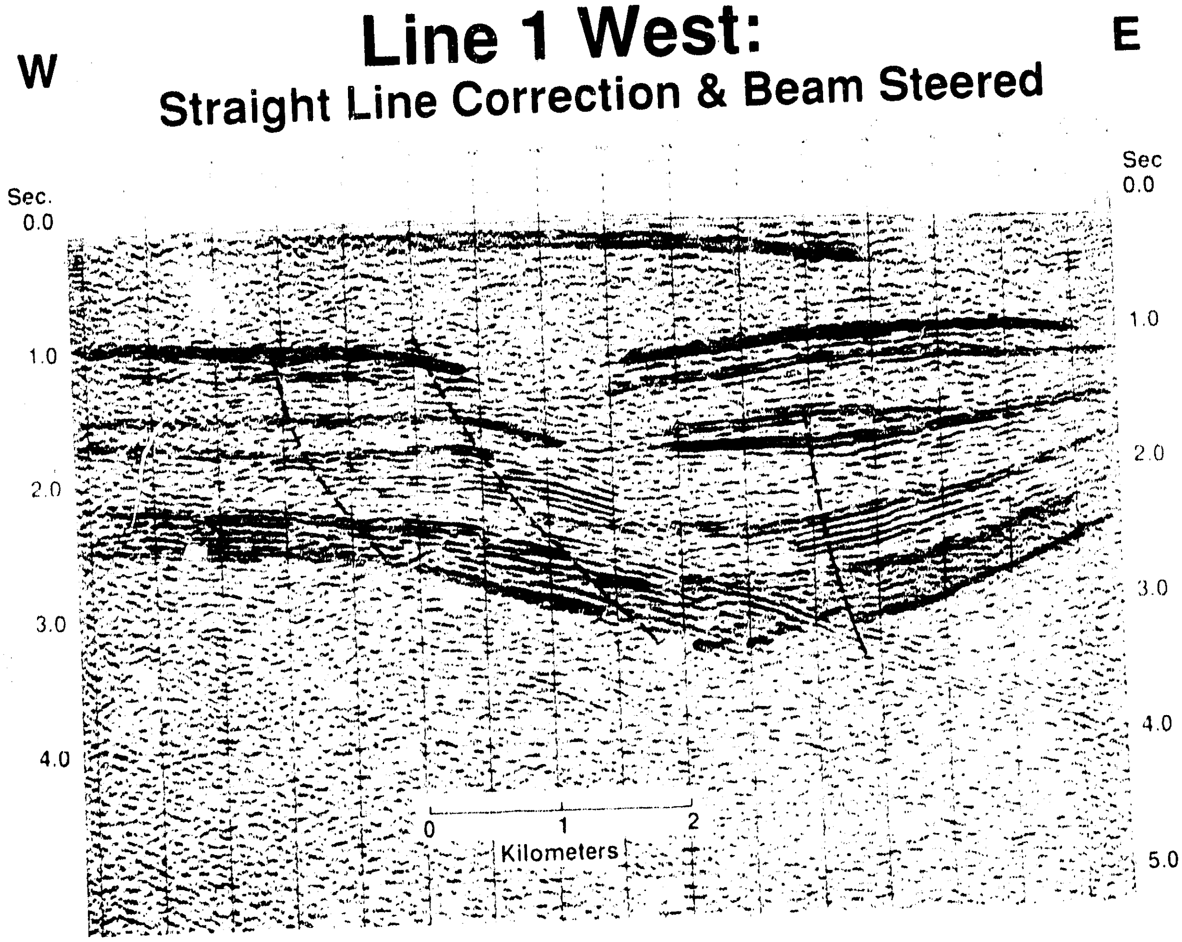

Figure 12. Straight-Line Correction and Beam-Steered Seismic Section for Line 1 Interpreted as a Rifted Basin

displays the seismic section, and while it does not provide significant improvement in imaging the postulated subduction layer, it does provide an offset seismic line usable in constructing a three-dimensional section for the subsurface so that formation correlations can be resolved.

RIFTED BASINS, AN ALTERNATIVE HYPOTHESIS TO SUBDUCTION

The alternative hypothesis to the subduction hypothesis, which has subduction layers near the surface, is that basins like the Chehalis may be "pull-apart" or rifted basins related to major right-handed strike-slip faults. The Straight Creek Fault, north and slightly east of the survey area, is well-documented, and several other probable strike-slip faults off the coast have been recognized (Snavely and others 1980). A major strike-slip fault has been mentioned, which Johnson (1984) postulates passes through the San Juan Islands, through Puget Sound, and possibly terminates in the area of southwestern Washington. Pull-apart basins can be an attractive exploration target for hydrocarbons in that reservoir-quality, deep-water sands may be found in conjunction with source beds that have undergone thermal maturity. Possible large structures for hydrocarbon entrapment are the Morton anticline, the Skate Mountain anticline, and

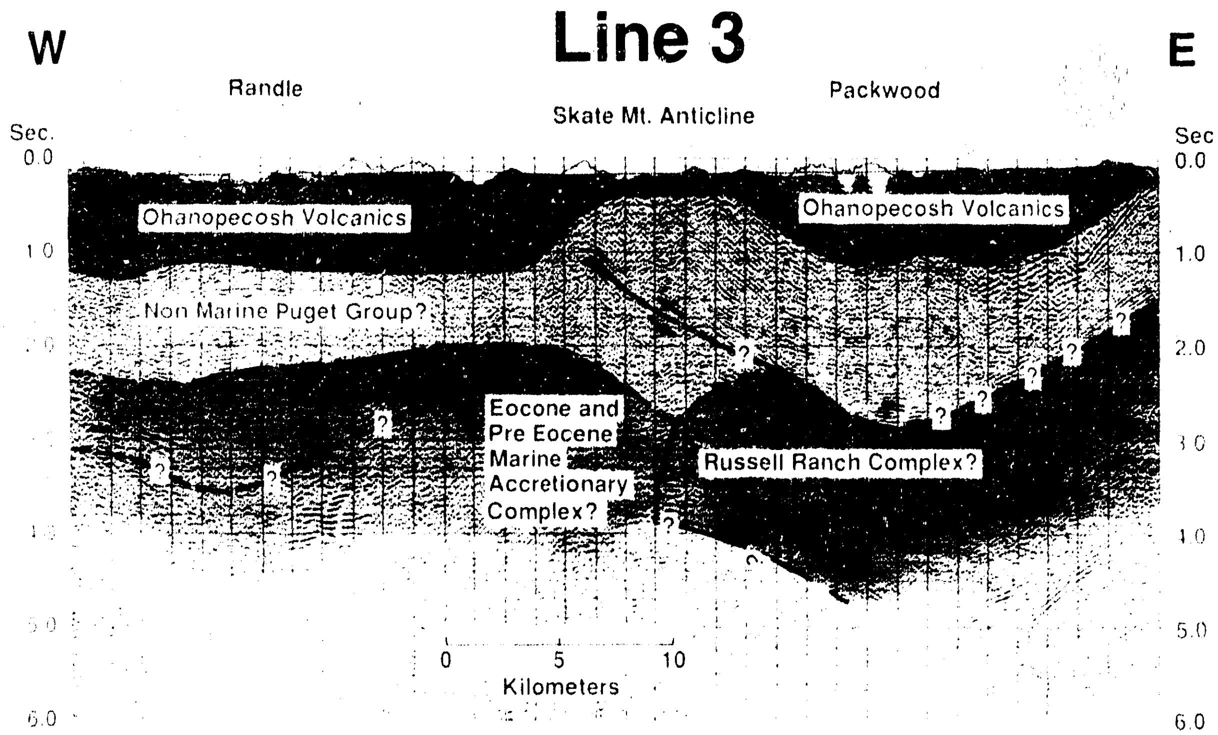

Figure 13. Seismic Section for Survey Line 3 Showing the Skate Creek Anticline

other faulted structures that have been mapped in the survey area.

SIMULATION MODELS FOR THE ALTERNATE HYPOTHESES

The seismic reflection method typically generates a profile that represents a corresponding cross-section of the subsurface geology. In complex areas such as southwestern Washington, the seismic response is actually a combination of the desired primary reflectors, noise, and artifacts of the seismic reflection method itself. These artifacts contaminate the geological representation, and the explorationist must separate the events as much as possible and identify the actual geological component. Computer models help to unravel these interrelationships by generating responses of various geological interpretations, which can be compared to the actual data. Because the mathematical procedures used for the modeling procedures are simplifications, the results of such model studies are never definitive. However, they are instructive and can add credibility to the final interpretation of the data.

For this study, the area near the Morton Anticline was modeled in two ways, one representing an abandoned subduction complex and the other a rift basin. The shallower reflectors of the model were designed

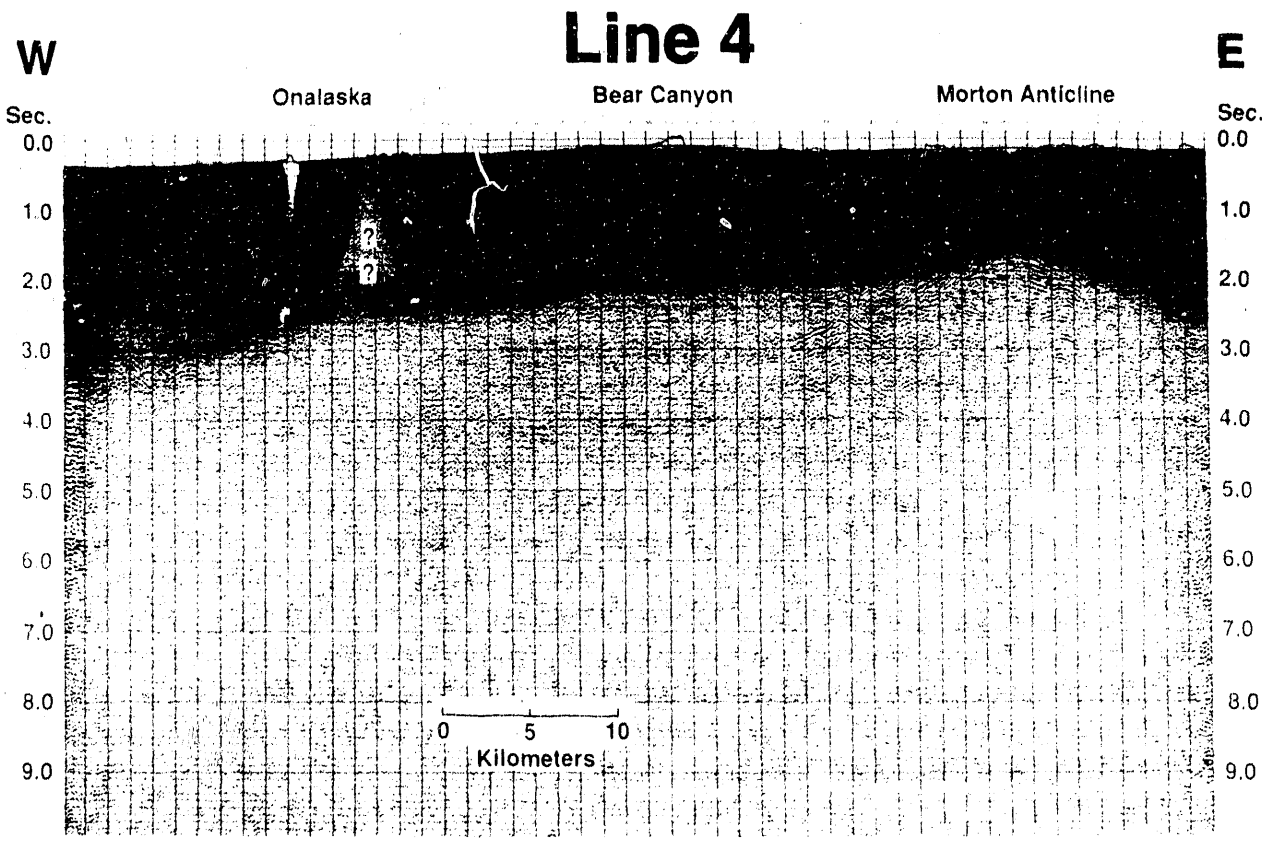

Figure 14. Seismic Section for Line 4 Crossing the Morton Anticline and Near Bear Canyon (McIntosh Formation Exposure)

to closely match the data as recorded on the two beam-steered line segments, Lines 1 and 2. The major differences occurred in the lower sections of the models, where an eastward-dipping reflector could be seen on the field data, which becomes indistinct beneath the Morton anticline. Layer velocities were used that are reasonable for the projected lithologies and depths. A seismic wavelet, made up of frequencies consistent with those generated by the vibrators, was used as the source wavelet and propagated through the models, creating simulated reflections as would be recovered in an actual survey. The results for the first of the models, the subduction model, are shown in Figures 15 and 16. Figure 15 is the structural velocity model and Figure 16 is the seismic response representation using spike pulses to enhance the resolution of the reflectors. The second model shows the simulation done to image the model response if the structure is a rifted basin. Again, reasonable velocities are used (Figure 17) and spike wavelets are employed to enhance image resolution (Figure 18). Results of the study show a strong similarity between the two models. The deep event seen on the actual data as an eastward dipping reflector can be reproduced as the geophysical response of an asymmetrical syncline on the rift model (Figure 18). In

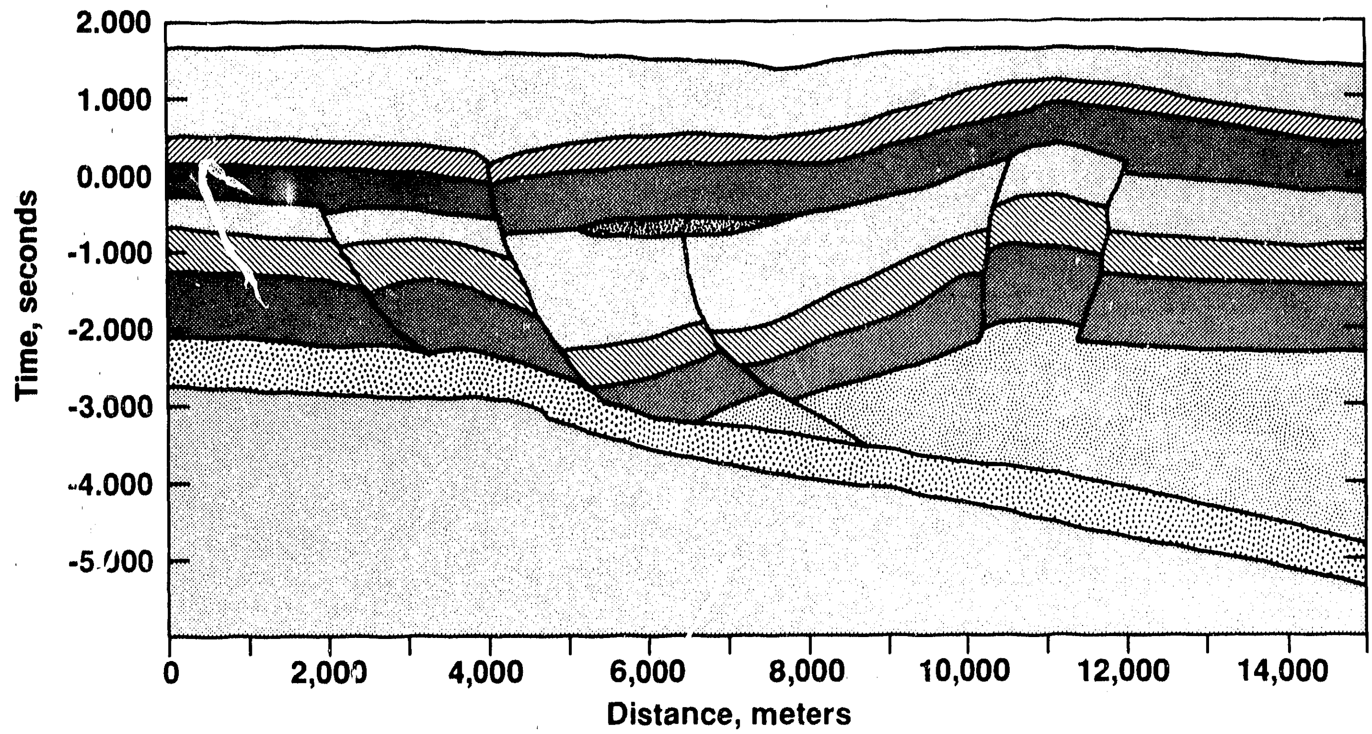

Figure 15. Subduction Hypothesis Geologic/Velocity Model

this case, it is essentially a geophysical artifact caused by the geometry of the rock layers.

The subduction model, Figure 16, which uses a shallow dipping layer meant to represent a "downgoing slab" for the lowest reflector, shows much the same character. Here, the slab reflector is visible across the length of the model, but the geological response of the Morton anticline has caused the seismic response at the downgoing slab to be distorted and irregular. On actual data, which has poor signal-to-noise characteristics, this reflector might be difficult or impossible to image. Furthermore, if the downgoing slab layer was modeled to have increasing dip beneath the Morton anticline, as is indicated from other geophysical surveys, energy from the most steeply-dipping events will be reflected off the end of the model and not recovered. In such a case, the model responses would effectively be identical.

Results of the modeling effort indicate the likelihood of a shallow basin to the west of the Morton anticline, but imply that a "downgoing slab" beneath this basin would be difficult to distinguish from a simple, asymmetric syncline. The presence of stratified reflectors within the Morton anticline is inconsistent with the interpretation that the imaged sediments are part of an accretionary prism. The interpretation of modeling results compared with field results favors the rift hypothesis, but final conclusions will depend on other information, such as well control, surface geology studies, or a better understanding of regional geological processes. The additional seismic survey data acquired

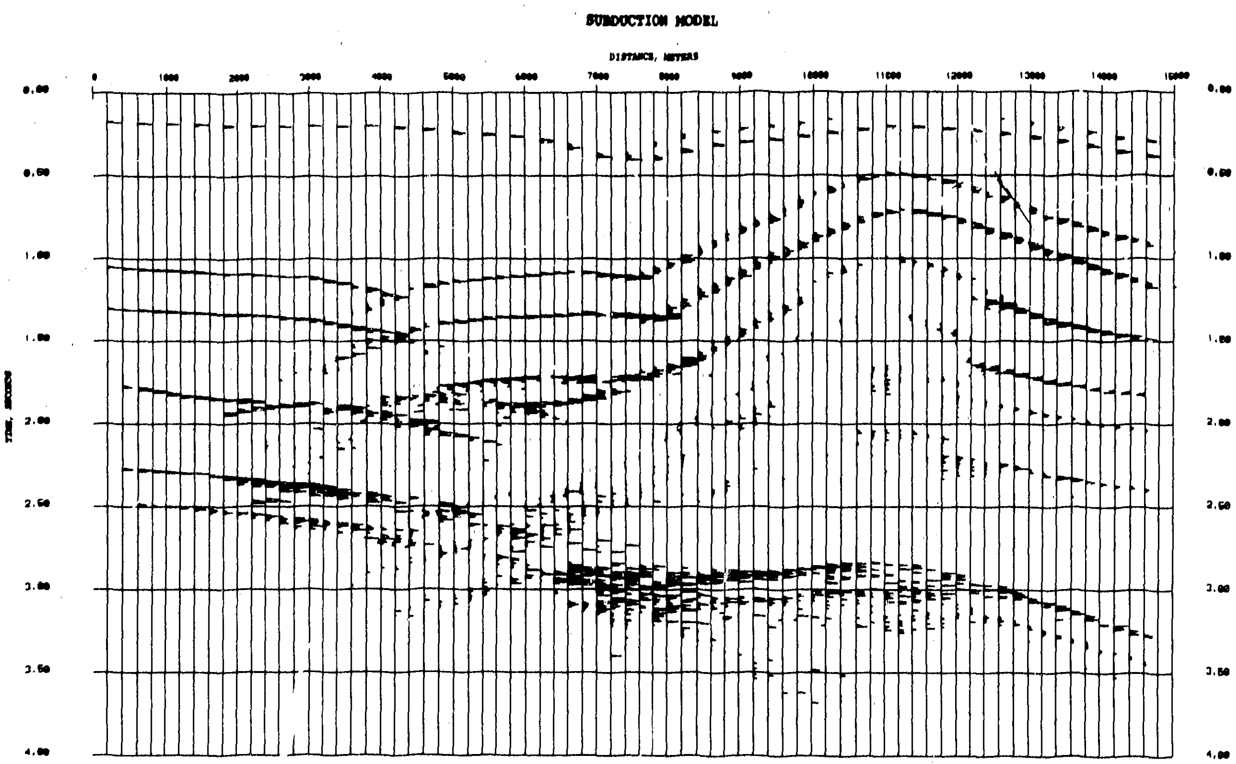

Figure 16. Seismic-Response Representation for the Subduction Model

in the summer of 1990 may provide better insight into resolving the ambiguity because of its orientation to the Morton anticline.

CONCLUSIONS

The processing, modeling, and interpretation of the 1988 and 1989 seismic surveys have yet to answer the question concerning whether or not the area west of and underlying the Morton anticline incorporates a subduction zone and associated accretionary prism sedimentary rocks as has been interpreted from the results of MT surveys. This interpretation also appears to be supported by other geophysical surveys such as gravity and magnetics. To help resolve these remaining issues, additional seismic surveys were run in the summer of 1990 over the key areas of interest as shown in Figure 8. A survey line was run approximately where Line 1 was surveyed using an improved source and detector array layout. In addition, a designed source array of dynamite explosions was used in an attempt to better resolve questions about the subsurface. This survey line has been designated Line 5 and has yet to be processed. A second survey line, Line 6, was run approximately 25 km north of Line 4 as shown in Figure 8 and followed an east-west logging road, which should yield a new imaged section of the western edge of the SWCC. Line 6 connects

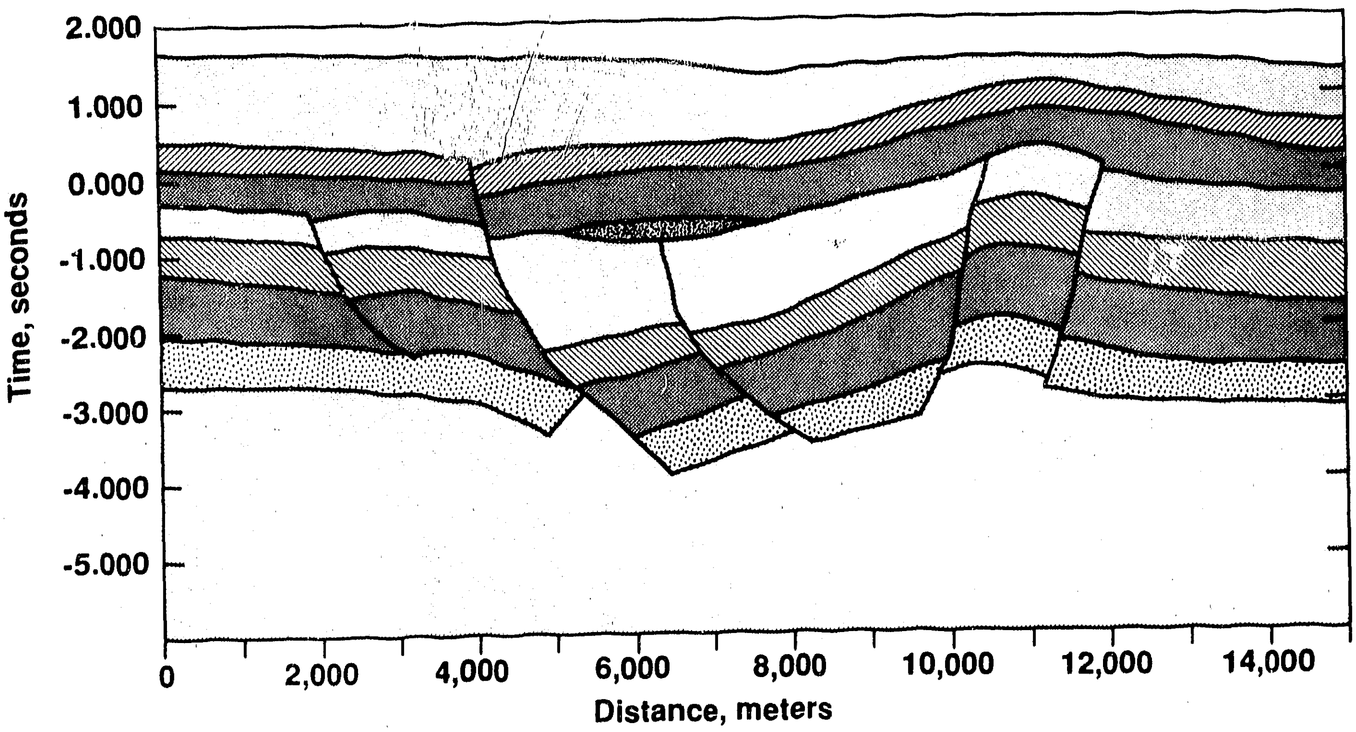

Figure 17. Rifted Basin Hypothesis Geologic/Velocity Model

on the east with the northern extension of Line 5 at the town of Elbe, Washington. It has yet to be processed.

To complement and aid in the subsurface interpretation of the resource area of interest, a contract has been awarded to accomplish detailed mapping of the structure of the Morton anticline and the adjacent anticlinorium. That work is nearly complete and will culminate in a report that discusses the potential for (1) source rocks in the area of interest, (2) the presence of reservoir rocks that may occur within sandstones of the McIntosh Formation, and (3) natural gas entrapment within structures such as the Morton and Skate Mountain anticlines. A key objective of the report will be to attempt to resolve the structural ambiguity of the region as to whether the major subsurface structure is associated with subduction or rifted basin tectonics or some combination. The discussed data will be integrated in the final report providing maps, sections, tabulations, interpretation, and the assessment of the potential for hydrocarbons to exist in this complex area of geology in southwestern Washington.

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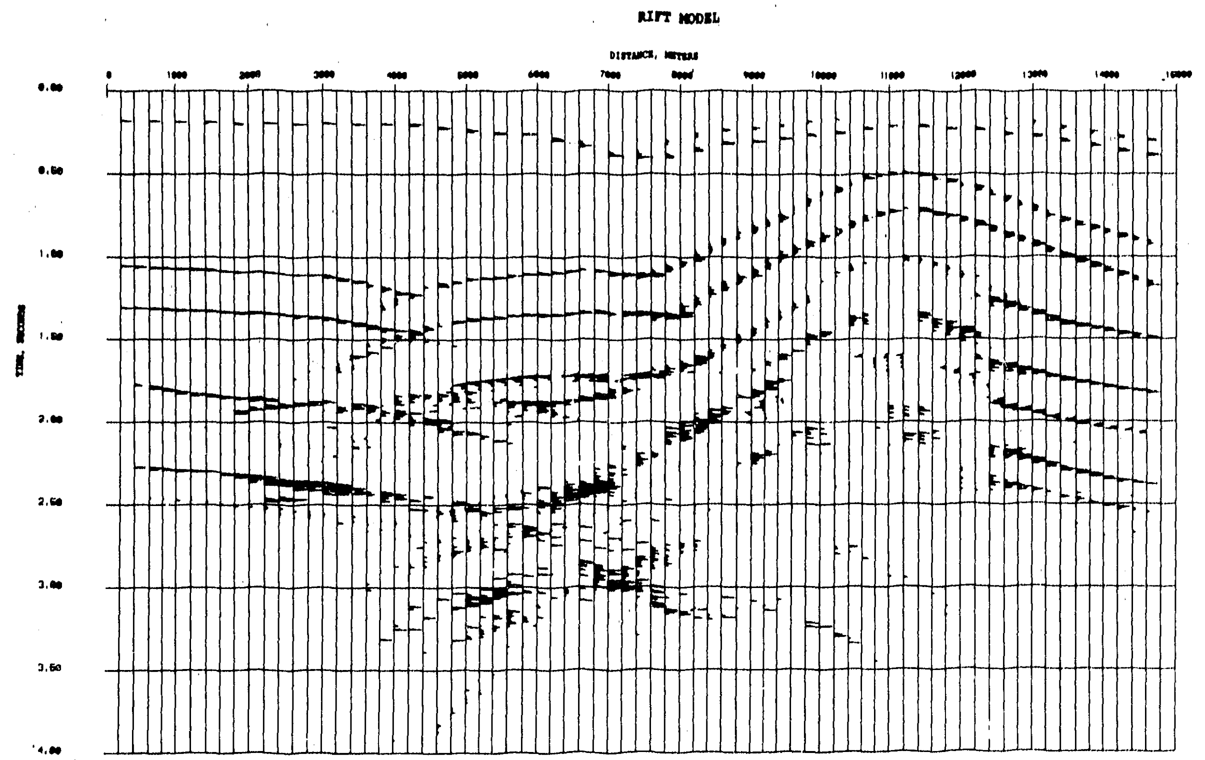

Figure 18. Seismic-Response Representation for the Rifted Basin Model

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Geophysical Reconnaissance for Deep Methane Source Rocks

CONTRACT INFORMATION

Contract Number Interagency Agreement DE-A121-83MC20422

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Period of Performance October 1, 1990 to September 30, 1991

Schedule and Milestones

FY91 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
Complete aeromagnetic/resistivity maps	●	-	-	-	●								
Complete AAPG manuscript		●	-	●									
Acquire/model detailed gravity data								●	-	-	●		
Prepare deep drilling proposals					●	-	-	-	●				

OBJECTIVES

The broad objectives of the activities under this task are to locate deep sedimentary complexes in the western Cordillera of the United States using deep investigative geophysical methods. Both reconnaissance and detailed surveys using magnetotelluric (MT) soundings have been coupled with gravity and magnetic data to locate geophysical anomalies that may represent deeply emplaced sedimentary rocks in fossil subduction zones or other structural settings. In FY90 the objectives were to provide further detailed geophysical investigations into the very promising southern Washington Cascades region where MT surveys outlined a possible sutured sedimentary complex beneath volcanic rocks. The proposed sedimentary complex is interpreted to correspond to an anomalous conductive region called the southern Washington Cascades conductor (SWCC). Recent deep seismic-reflection surveys have confirmed the structural style and probable lithology interpreted from the MT results and from aeromagnetic data. The focus of the FY91 studies will be on the Morton anticline, a primary st. uctural feature that brings the conductive rocks near to the surface. Aeromagnetic data has been invaluable in studying contacts between volcanic rocks and sedimentary rocks in the area; however, in the Morton anticline, the data is very poor because it was acquired on 6 mile flightline spacing for uranium surveys in the 1950's. The main field activities during FY90 involved acquisition of a new aeromagnetic data set covering the main part of the Morton anticline region, with east-west flight lines, 1000 feet above the ground, and with 1/2 mile spacing. This data will be compatible with other high-quality data available west, north and south of the study area and will allow compilation of a highly-improved regional aeromagnetic map covering the southern Washington Cascades and nearby Chehalis basin. In addition, airborne electromagnetic resistivity data were obtained simultaneously with the magnetic data to provide information on occurrences of conductive marine sediments in the near surface.

BACKGROUND INFORMATION

Convergent margins are the scene of the most dynamic of geological processes. Subduction at convergent margins acts as a conveyor belt for metallic minerals and carbon into the mantle and leads to concentration of large amounts on marine and continental organic material in sediments that form accretionary prisms and forearc basins. These large concentrations of organic material may be trapped in suture zones that occur when microplates riding upon the subducting oceanic crust arrive at the margin, subsequently compressing the sedimentary complexes and often leading to a outboard translation of the subduction zone. Such accretion-trapped sedimentary complexes offer a potential for large volumes of source rock at depths that may not be commercially accessible under normal conditions, but could play a significant role in supplying hydrocarbons to conventional reservoirs.

The complicated geological environment and frequent volcanic cover make exploration for sutured sedimentary systems very difficult, but success has been achieved in mapping these systems with deep electrical soundings, largely because of the large resistivity contrasts present. The sutured sedimentary rocks have very low resistivities compared to surrounding volcanic and metamorphic rocks in a suture zone; this fact has led to the application of magnetotelluric (MT) surveys to map possible unmapped sedimentary systems near convergent margins.

PROJECT DESCRIPTION

This project involves the use of geophysical methods in the western U. S. Cordillera to search for unmapped deep sedimentary complexes associated with fossil subduction zones, primarily of Mesozoic and Cenozoic age. These unmapped sedimentary complexes are viewed as a possible deep source of methane that could conceivably be reservoired at exploitable depths. Deep source methane in the Department of Energy is defined as methane originating deeper than 30,000 feet (9.1 km). Geophysical surveys in this project primarily rely on the magnetotelluric (MT) sounding method that measures earth resistivities using naturally occurring magnetic and electric fields as an energy source. These naturally occurring plane-wave signals are recorded with very sensitive, low-noise magnetometers and electric-field sensors and processed with an in-field computer system to determine earth resistivity versus frequency. From this spectrum of resistivity versus frequency, determined as a tensor quantity, one can resolve the earth's electrical structure in terms that can be related to lithology and structure in one-, two-, and three-dimensions. The measurement of resistivity is particularly effective because of the large dynamic range of this physical property in rocks, where carbonaceous shales with marine fluids may be typified by resistivities of 1-3 ohm-m and intrusive, granitic rocks may be >10,000 ohm-m. Other rocks units have characteristic resistivities, and although various units may overlap in resistivity, the ability of resistivity measurements to determine lithology, particularly the presence of marine sedimentary rocks, is much greater than that of seismic or potential field (gravity and magnetic) methods.

MT surveys in this project have been carried out largely in the Pacific Northwest and parts of California and Alaska during the course of the project research. In the Pacific Northwest and in Alaska, concurrent or subsequent deep seismic reflection surveys have been completed that add additional information. In some instance, magnetic and gravity data have been instrumental in understanding geological structures. After completion of an a extensive reconnaissance of the Mesozoic subduction complexes in the Pacific Northwest and the study of a large compressed flysch basin in Alaska, focus has been on a possible sutured accretionary prism/forearc basin complex located with MT surveys in the southern Washington Cascades region. Extensive deep seismic reflection and other studies have been done in the latter area under auspices of the Morgantown Energy Technology Center in the last three years. Results from this study area are described in the next section.

RESULTS

A short summary of results is followed by details of the southern Washington Cascades study:

- An MT survey of the Mesozoic subduction complex in the Blue Mountains, Oregon showed that there were no deeply rooted sedimentary complexes. Jurassic black shales and sandstones that are most interesting from a source-rock standpoint were found to be relatively thin and did not exists below depths of about 3 km.

- MT surveys and gravity/magnetic data in the Roseburg, Oregon area show that an early Cenozoic suture zone with known oil seeps does not presently contain large volumes of source rocks and is bordered by extensive Tertiary magmatic arc intrusives. The oil seeps may represent hydrocarbons sourced from Tertiary marine sediments, or remnant oil from Mesozoic sediments heavily intruded by magmatic arc intrusives.

- A study of the Mist gas field and surrounding Oregon Coast range using MT surveys and gravity/magnetic data indicates that no unmapped deep sedimentary rocks exist in the Mist area. Structures in the Coast Range are largely related to "blockiness" of the seamount complexes that comprise this province; some thrusting of individual Coast Range blocks was mapped, but no entrapped sedimentary units of significant thickness are included in the thrust plates, except at depths greater than 20 km (related to the current subduction zone).

- Mapping of a large compressed flysch system in Alaska (Stanley et al., 1990a) has been done as part of the DOE Deep Source Gas Project and the USGS Trans-Alaska Crustal Transect (TACT) program. It has been found that much of the Yukon-Tanana crystalline terrane in central and eastern Alaska may be underplated with black shales derived from a very extensive flysch belt that existed along the Alaskan-Canadian borderland during late Jurassic and early Cretaceous. Evidence for this hypothesis includes MT models (Stanley et al., 1990a), seismic reflection data (Fisher et al., 1988), Pb and Sm-Nd isotope data (Aleinikoff et al., 1989), and extensive geological information (Nokleberg et al., 1988).

- A literature and colleague study of worldwide geologic analogs have played a key role in understanding possible deep sedimentary systems in the western U.S. Cordillera. Specifically, comparisons have been made of the Alaska and Washington sedimentary complexes with compressed flysch systems in the eastern Alps and Carpathian Mountains of Europe (Stanley, 1989).

- The nature of deep conductors in convergent margin regions has been better understood with the recent integration of several regional MT and seismic refraction profiles in the Cascades. This combined interpretation shows that the crust throughout the Cascades is normally quite layered, except where a major conductivity anomaly occurs in the southern Washington Cascades. Midcrustal conductors coincident with slightly higher refraction velocities and a pseudo-horizontal attitude were interpreted to be caused by metamorphic fluids (Stanley et al., 1990b).

Southern Washington Cascades Conductor

The main focus in the past three years has been on southern Washington Cascades region. Geophysical and geological studies in the southern Washington Cascades have outlined a possible, previously unmapped, complex of sedimentary rocks. These postulated sedimentary rocks are interpreted as corresponding to at least the upper section of a low-resistivity package at depths of 1 to 10 km and with thicknesses of up to 15 km that we call the southern Washington Cascades conductor (SWCC). The upper surface of this conductive complex correlates in some places with surface anticlinal structures that bring Tertiary marine rocks near the surface. These anticlinal structures have been imaged in detail with deep reflection surveys. The conductive rocks were traced to the surface west of Morton, Washington where they correlate with shales of the lower Eocene McIntosh Formation. We interpret that the conductive package is largely related to such Eocene, and older, marine sedimentary rocks. Other possible lithologies for the conductive package have been considered in detail. Although paleotectonic and petrologic considerations favor marine sedimentary rocks as the primary constituent of the SWCC, parts of the complex may be composed of continental sediments like those in the upper part of the deltaic-origin Puget Group or those in nearby pull-apart basins. Geothermal fluids are possibly a contributing factor to low resistivities in the deeper parts of the complex (greater than 6-7 km). Another possible candidate for the conductive units is a thick section of highly-altered volcanic flows. Also, the possibility exists that the anomalous rocks are composed of pre-Tertiary sedimentary or carbonaceous metamorphic rocks.

Seismic reflection data acquired along U.S. Highway 12 outline internal structure of the Morton anticline, a key feature previous mapped with the MT surveys. Pseudo-horizontal, high-amplitude reflections in the core of the anticline may be indicative of pore-fluid anomalies, possibly gas or high-pore-pressure hydrous fluids, although attribute analysis must be completed before these events can be fully analyzed. A deep, east-dipping reflector was mapped roughly coincident with the position of resistive basement rocks from the MT surveys. This basement is postulated to represent the basal oceanic crust beneath the presumed sutured accretionary prism/forearc complex. Other, possibly significant, anticlinal structures, such as the Skate Mountain anticline, were mapped in clear detail on the reflection data after earlier being observed with less clarity in MT surveys.

Paleotectonic analysis of the postulated marine sedimentary complex suggests that, if the conductive rocks are derived from an accretionary prism/forearc basin system, they could have been favorable sources for hydrocarbons (Stanley et al., 1991). The seismic and MT results show that possible anticlinal traps (of unknown three-dimensional closure) may exist above the main parts of the proposed sedimentary complex. However, high crustal heat-flow caused by Oligocene to Recent magmatic arc activity probably has left most of the proposed sedimentary complex in an advanced state of thermal maturity. Timing of the formation of the anticlinal structures with regard to the thermal events is the key factor in determining the hydrocarbon potential of the hypothesized sedimentary systems. The geophysical surveys have outlined key locations for stratigraphic testing needed to determine the lithology of the anomalous section and its hydrocarbon potential.

FUTURE WORK

Key tasks during FY91 for this project include completion of airborne magnetic and electromagnetic resistivity maps from data acquired in FY90 with U.S. Geological Survey aircraft and instrumentation. The magnetic and electromagnetic resistivity maps of the Morton anticline and other features should be valuable in determining the structural axes of the anticline and surface lithology where geological mapping information is limited. A manuscript has been prepared (Stanley et al., 1991) that synthesizes all of the available geological and geophysical information for the SWCC region and its significance to the hydrocarbon potential. This manuscript will be both open-filed and submitted for journal publication. During the 1991 field season, detailed gravity profiles will be obtained coincident with the seismic reflection and MT transects across the Morton anticline. The models derived from these gravity data should be useful in providing constraints on the hypothesized oceanic crust beneath the SWCC in the Morton anticline region. Deep drilling proposals are being prepared to initiate stratigraphic and research drill tests of the SWCC region.

Deep seismic reflection results have been somewhat disappointing in the SWCC region in that details of the geology below about 3 seconds two-way travel-time (depths of approximately 6-9 km) are largely missing. A plan to utilize wide-angle reflection/refraction surveys using dynamite sources to map deep structural features missing in the standard, vertical incidence reflection data is in development within the U.S.G.S. These surveys would use wide-angle, fan-shooting and other techniques to record post-critical (large amplitude) reflection from horizons such as the proposed oceanic crust beneath the SWCC, only marginally seen in the Vibroseis data. Three-component seismometers would be used to record shear-wave energy as well as compressional events; P and S-wave velocity information obtained would greatly aid geological interpretations.

As a long-term goal, dependent upon funding, the project will continue to investigate massive amounts of black shales that are interpreted to occur beneath the Yukon-Tanana terrane in Alaska, where seismic reflection data show possible bright spot indicators. Also, the potential for deep source rocks in the Yukon Flats region and southern Brook Range of Alaska needs to be studied with MT surveys and other geophysical data for integration with past geological studies by David Howell, U.S.G.S., and others. Continued geophysical research in the Roseburg, Oregon area mentioned above is needed to complement geological and geochemical research on hydrocarbon occurrences being done by the State of Oregon, the French Petroleum Institute, and U.S.G.S. Office of Regional Geology.

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Potential for Natural Gas Resources in Deep Sedimentary Basins

CONTRACT INFORMATION

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Period of Performance:	July 12, 1990 to September 30, 1990	

Drilling and production data from deep (greater than 15,000 feet) wells and reservoirs in sedimentary basins of U.S. indicate that deep gas is an important energy resource (Figure 1). More than 16,000 wells have been drilled to depths greater than 15,000 feet (Figure 2). At least 3,000 of these wells are definitely producing hydrocarbons from below 15,000 feet. The percentage of gas wells versus total producing wells increases with depth from a minimum of 72 percent at 15,000 feet to more than 90 percent at 19,000 feet. The deepest established production is at 26,566 feet, whereas the deepest well reaches a total depth of 31,236 feet. This difference between deepest production and total depths may be due to lack of reservoirs and gas quality. Although gas, in particular methane, is stable at high levels of thermal maturity, reservoir quality (porosity and permeability) generally decreases with increasing time-temperature exposure, except where secondary porosity and/or natural fractures are developed. In addition, gas quality commonly decreases with thermal maturity. Nonhydrocarbon gases, such as H_2S and CO_2, can dilute and even destroy deep methane accumulations.

As of 1985, approximately 50 Tcf of gas had been produced from deep reservoirs in the U.S. This deep gas production accounts for about 8 percent of the U.S. cumulative production (700 Tcf). The Gulf Coast (East Texas, western Gulf, and Louisiana-Mississippi salt basins) and the southern mid-continent (Anadarko, Delaware, and Val Verde basins) regions account for 95 percent of the cumulative deep hydrocarbon production. Deep production has been established in Cambrian through Tertiary clastic and carbonate reservoirs. About 75 percent of deep gas wells produce from clastic rocks.

The Potential Gas Committee (1989) estimated that 33 percent of the undiscovered gas resources in the U.S. occurs at depths greater than 15,000 feet. The most favorable areas for deep gas potential are the Gulf Coast (East Texas, western Gulf, and Louisiana-Mississippi salt basins) and the mid-continent (Anadarko, Arkoma, Delaware, and Val Verde basins) regions where most of the deep wells have been drilled and deep gas production has been established, and the Rocky Mountain area (Green River, Uinta, and Wind River basins) where geologic conditions are favorable for deep gas accumulations, but regional pipelines have not been built.

The Gulf Coast region, located both onshore and offshore, is a passive continental margin with active growth faults and salt and shale flowage that have resulted in abundant structural traps and provided conduits for the movement of hydrocarbons and other fluids. These factors, in addition to others, have given the province all of the ingredients necessary for making it one of the nation's most important areas for both discovered and undiscovered hydrocarbons. In addition, the province has an enormous volume of sediment deeper than 15,000 feet and is considered to have the best potential in the U.S. for undiscovered resources of deep gas. The deep gas potential is large not only for conventional resources, but also for unconventional resources, such as geopressured methane and gas from low-permeability (tight) reservoirs.

The Gulf Coast region has the largest number of deep wells in the conterminous U.S., and deep gas production has been established in several important trends, including Paleocene Wilcox in southern Texas, Lower Cretaceous Tuscaloosa in southern Louisiana, Upper Jurassic Smackover in Mississippi and Alabama, and Upper Jurassic Norphlet in southern Mississippi and Alabama. The deep Tuscaloosa, Smackover, and Norphlet reservoirs are characterized by abnormally high porosity and permeability for their depth of occurrence.
The potential for undiscovered deep gas accumulations exists in both clastic and carbonate reservoirs ranging in age from Jurassic to Pleistocene. Potential from the oldest rocks is along the inner rim of the province, with the productive trends becoming younger in a seaward direction.

In spite of enormous amount of data generated from the drilling of wells and production of hydrocarbons, a publicly available data base and regional synthesis of the petroleum geology is absent, including that of the deeply buried gas-bearing section. To properly evaluate the deep gas potential, the geologic framework should be established with emphasis on the major reservoir, seal, and source rock units, and the definition of traps. This reconstruction can be completed using previously published reports and analyzing logs, samples, and cores. A computerized data base will be established to aid in this evaluation.

The U.S. Geological Survey, in cooperation with State agencies and with the support of the U.S. Department of Energy, will initiate a program of research to determine the geologic framework and processes controlling deep gas occurrence in onshore part of Gulf Coast province. Although deep gas potential exists offshore, the onshore data are publicly available and much information is available in public literature. The study area will be the Louisiana-Mississippi salt basins (including Alabama). At the request of DOE, the USGS will work with the State agencies in developing a computerized data base of subsurface information that can be used for reconstructing the petroleum geology and will serve as a basis for evaluating the potential. The project will result in the publication of geologic reports, such as regional cross sections and maps, analyses, and interpretations of thermal maturity, reservoir properties, natural gases, and source rocks and discussions of processes involving basin evolution, reservoir and trap development, thermal history, and hydrocarbon generation, and migration that have direct bearing on the distribution and resource potential and eventual exploitation of deep gas resources.

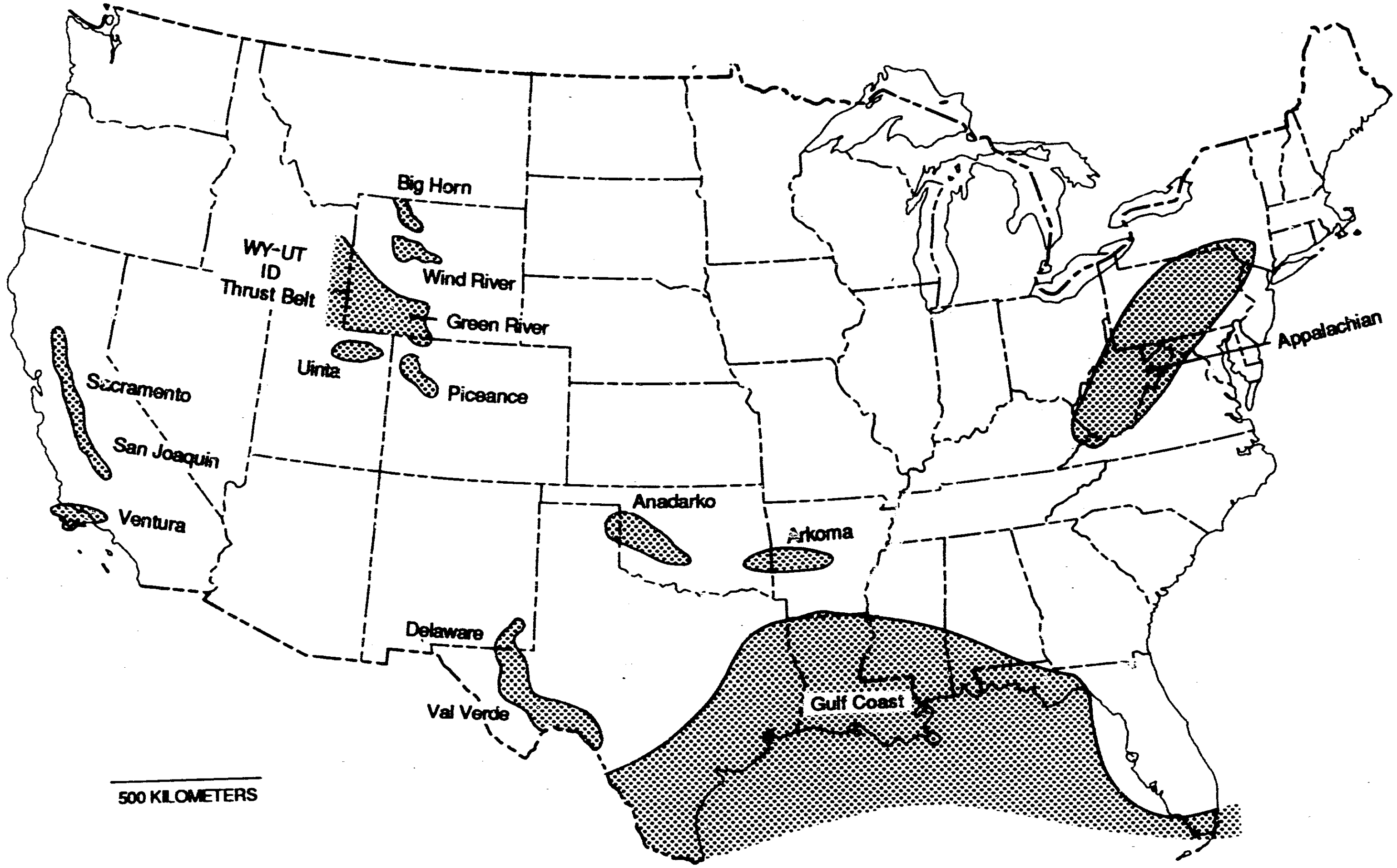

Figure 1. Map of Coterminous United States Showing Parts of Basins with Significant Volumes of Sedimentary Rocks Greater Than 15,000 Feet.[1]

[1] Modified from Rice (1989).

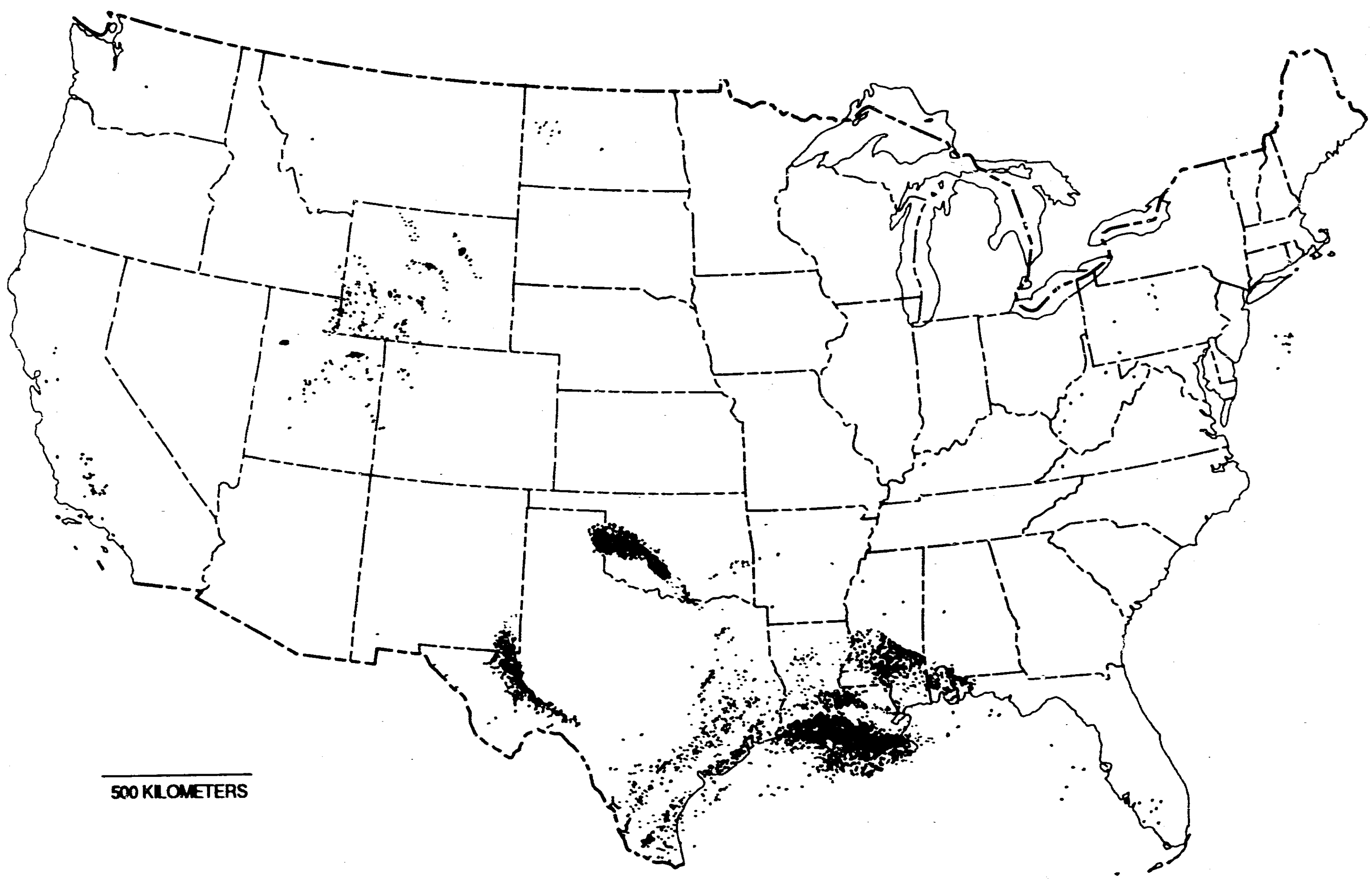

Figure 2. Map of Coterminous United States Showing Approximate Location of More Than 16,000 Wells Drilled to Depths Greater than 15,000 Feet.[1]

[1] Modified from Tokahashi and Cunningham (1987).

Kinetic Models of Hydrocarbon Generation

CONTRACT INFORMATION

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Period of Performance	April 1, 1990 to March 31, 1991

OBJECTIVES

We are carrying out an integrated program of laboratory experiments, kinetic modeling, and basin thermal history modeling in order to better understand the natural breakdown of organic matter into oil and gas. Our kinetic models of organic maturation are being used to better understand the coupling of generation, cracking, expulsion, and overpressuring in both the laboratory and geologic setting. Currently we are carrying out chemical experiments and developing more efficient chemical kinetic modeling schemes to obtain a better understanding of expulsion and cracking from lean source rocks and from hydrogen-poor (terrestrial) organic source material. We verify the chemical kinetic models by integrating them with thermal history models of hydrocarbon-producing sediments and comparing predicted and observed characteristics of the hydrocarbon occurrence in a variety of settings. We intend to apply this approach to evaluate the potential for deep gas resources in the Pacific Northwest and in the Louisiana Gulf Coast.

BACKGROUND INFORMATION

It is now widely appreciated that oil and gas generation is governed by chemical kinetics describing the breakdown of more complex organic matter. LLNL has been in the forefront of efforts to develop a quantitative description of this process. Gas can be generated either from cracking of oil that cannot migrate to a cooler reservoir above or from hydrogen-poor kerogens, including coal and residual oil-prone kerogens. Both processes occur at a greater depth (temperature) than oil generation. Such depths will probably be greater in the convergent margin setting than in the deep basin setting because of the differences in the thermal regime. The precise kinetics of gas generation are less well known than for oil generation. Recent research at LLNL has suggested that oil-prone source rocks, when lean (less than 1%-2% total organic carbon), will be primarily gas producers because there isn't enough driving force to expel the oil before it is cracked to gas. Sediments in convergent margins are generally lean and gas-prone. It has been proposed that a significant amount of the hydrocarbons produced in the onshore and offshore U.S. gulf coast sedimentary basin originated from lean source rocks.

Models of gas generation should also include the calculation of overpressure (pore pressure in excess of hydrostatic) because it is a measurable phenomenon that can be used in calibrating the model, it is an important mechanism for preserving porosity in deeply buried sediments, and it is important to predict for the driller. We have developed a pseudo 1-D model of pore pressure that includes chemical generation kinetics, gas-oil equation-of-state calculations, and a simple compaction model of sediments. We are improving this model by incorporating the effects of thermal expansion of water, mineral transformations, and dehydration and couple these with calculations of the solubility of gas in water.

We use basin modeling (determinations of the time-temperature history of sediments) in combination with the chemistry to determine if, when, and where hydrocarbons are generated as well as to check the chemical models. In general, the level of detail of the basin model is determined by the quantity and quality of stratigraphic, age, structural, and physical property data available for the sediments. At one end of the range of complexity, thermal history modeling can involve using simple estimates of geothermal gradients, either assumed or based on bottom-hole temperatures, that are assumed to be constant through time. At the other end of the range are integrated 2-dimensional fluid-flow and conductive heat flow calculations that require a great deal of knowledge about physical properties and local structure.

PROJECT DESCRIPTION

In order to examine the characteristics of possible deep gas generation in a convergent margin we will develop a preliminary thermal model for sediments beneath the recently-obtained seismic line in Washington and Oregon using the seismic data and any other pertinent data available. Following this, we will make preliminary estimates of oil and gas generation in the convergent margin of the Pacific Northwest using existing organic geochemistry models. To carry out improvements (mentioned above) to PYROL, our general hydrocarbon modeling code, and to PMOD, a code similar to PYROL but with simpler PVT calculations and a highly flexible reaction scheme, we will acquire geochemical data and source rock samples for analysis and laboratory experiments and couple this work with detailed thermal history modeling in an area where a lot of data are available and the geologic history is relatively straightforward. These criteria are best met in areas of the onshore U. S. gulf coast where there has been extensive drilling, exploration, and recovery of hydrocarbons. A wealth of data is available for the onshore gulf, where some tentative identification of source rocks has been made. This contrasts with the offshore gulf, where nonproprietary data is limited and the identification of source rocks for the hydrocarbons recovered there is a major unresolved problem. We choose the onshore gulf also because, like the convergent margin of the Pacific Northwest, some of the source rocks are thought to be lean and gas prone. With this approach, coupled with improved thermal history modeling of the convergent margin of Washington and Oregon, we can accomplish three major objectives:

(1) refine our ability to characterize the generation of gas at moderate and deep levels in lean and rich source rocks of all types.

(2) apply the refined modeling capabilities to better characterize the gas reservoir potential at deep levels in convergent margins.

(3) attempt to solve major unresolved problems about hydrocarbon generation and migration in the onshore and offshore U.S. gulf coast.

RESULTS

PYROL was originally developed to aid in the understanding of chemical processes involved in retorting of lacustrine oil shale of the Green River Formation. Use of the model in the geologic setting was tested in the Uinta Basin (Sweeney et al., 1987). With recent laboratory and modeling work we have developed preliminary chemical kinetic parameters to model oil and gas generation in the prolific marine kerogen of the La Luna Formation and have tested this approach in the Maracaibo Basin (Sweeney et al., 1990).

Our experimental program is designed to use the simplest and most efficient methods to better understand the chemical processes and to determine the chemical kinetic parameters needed to model generation and cracking of hydrocarbons in conditions relevant to both the laboratory and nature. We continue to develop and improve our modeling capabilities with PYROL and now with PMOD so that they can more accurately predict the characteristics of oil generation, expulsion, and cracking to gas from marine and terrestrial kerogens. To guide further development, these models are continually being tested by comparing predictions with data under laboratory and natural conditions.

Chemical Analyses and Modeling

We have recently completed (Reynolds et al., 1990) a series of pyrolysis - triple quadrupole mass spectrometry (Py - TQMS) experiments, at heating rates of 10°C/min, on 15 different shale source rocks. Included in this group was a terrestrial source rock, referred to as JNUS, with a relatively low TOC of 1.5%. The evolution profile for the C_1-C_4 hydrocarbons is shown in Fig. 1. The T_{max} of each species, shown for each profile, is shown to be highest for methane, CH_4. All of the shale samples produce roughly the same total volumes of C_1-C_4, with CH_4 usually making up the largest volume of the species. The important result for the JNUS sample was that its pyrolysis yields are similar to pyrolysis yields for both the Argonne (Burnham et al., 1989) and Brent (Espitalie et al., 1988) coals. These results

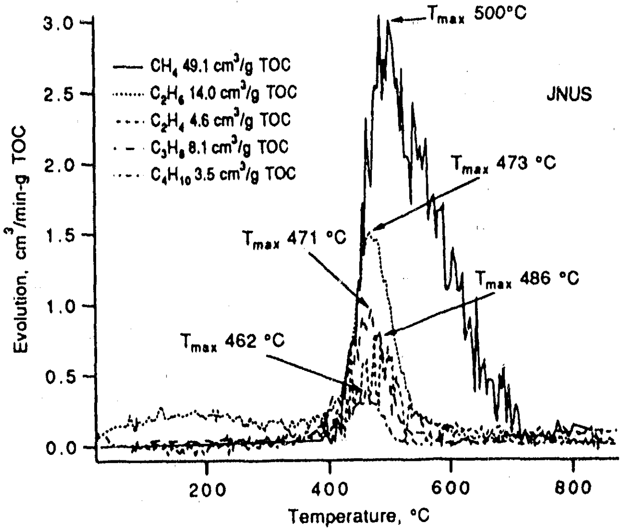

Figure 1. CH_4, C_2H_6, C_3H_8, and C_4H_{10} evolution profiles for a lean terrestrial kerogen at 10°C/min heating rate. T_{max} for each profile is indicated.

suggest that TOC of the source rock does not greatly affect the relative yield (normalized to TOC). These methane evolution profiles are also similar to that calculated from vitrinite with our VITRIMAT kinetics (Burnham and Sweeney, 1989).

Although we have not developed a detailed maturation model for Type III kerogens, our VITRIMAT model does represent a starting point. We have tested the ability of VITRIMAT to calculate the increase in T_{max} of methane and total hydrocarbons with increased vitrinite reflectance (%R_O). Recently, Whelan et al. (1990) investigated methane evolution as a function of thermal maturity for two sets of isolated terrigenous kerogens using thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR) techniques. The bold and solid lines in Fig. 2 give the predicted dependence of methane T_{max} on %R_O for geological maturation at 1 °C/m.y. and T_{max} measurement at 30 °C/min. The bold line used the correlation between %R_O and H/C and the solid line used the correlation between %R_O and weight percent C. The lines are parallel but generally lower than the experimental values for two kerogens. The calculated relationship between %R_O and T_{max} of total hydrocarbons (not shown) starts about 10 °C lower but merges with the methane curve when %R_O reaches about 1.5. In contrast, the measured relationship for total hydrocarbons (as corrected for temperature calibration and heating rate) reported by Teichmuller and Durand (1983) falls about 50 °C below our calculated relationship. Although these discrepancies indicate that further measurements and model refinement are needed, the qualitative agreement between VITRIMAT and these experiments is encouraging.

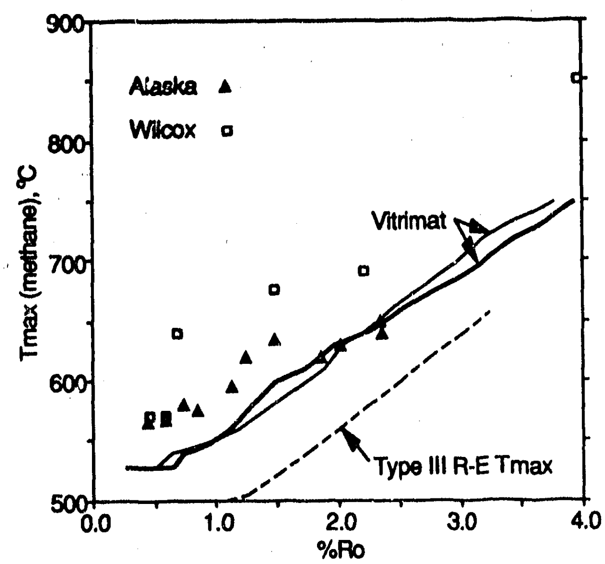

Figure 2. Comparison of calculated and measured T_{max} of methane as a function of vitrinite reflectance. Data from Whelan et al. (1990).

Another area of uncertainty in our current modeling is the stability of oil at great depths. In recent work in collaboration with Dr. R.L. Mallinson of the University of Oklahoma Chemical Engineering Department, we constructed a detailed free-radical model of butane cracking and used it to assess the importance of pressure on the cracking rate at geological conditions. Butane is large enough to have many of the chemical properties of oil but small enough to model in a detailed fashion. We used the model to investigate the cracking rate at temperatures from 200°C to 600°C and at pressures from atmospheric to 100 MPa. For a typical geothermal gradient of 25°C/km, a depth of 7 km corresponds to 200°C and about 80 MPa. Model calculations over this wide range of conditions show that the effect of pressure depends strongly on temperature. The overall rate of butane cracking is dramatically increased by elevated pressures at 600°C but shows the opposite behavior at 200°C. Simulations at temperatures of 300-375°C, the lowest at which the reaction is fast enough to be characterized by laboratory experiments, show that pressure can either accelerate or inhibit the reaction rate depending on the precise temperature and extent of reaction.

Applications to Geologic Settings

We used the thermal history model of Armentrout and Suek (1985) for the Mist Field in Oregon to compare predictions of their time-temperature index (TTI) model to those of our preliminary kinetic model for oil and gas generation (Burnham and Sweeney, 1990), which uses the same methane generation kinetics as in VITRIMAT. We assumed Type III (terrestrial) kerogen for the source organic material in the Cowlitz and pre-Cowlitz formations. The preliminary results show that most of the present-day generation of hydrocarbons, especially gas, in the Mist Field is occurring at depths greater than 15000 ft, far below the depths of production in the relatively shallow reservoir sandstones. This result, which is somewhat more quantitative than the previous work, agrees in principle with the suggestion of Amentrout and Suek (1985) that the gas in the field had migrated there from greater depths.

In another preliminary study, we have been trying to develop a thermal history, constrained by vitrinite maturation data and using our vitrinite maturation model (Sweeney and Burnham, 1990), for the Phillips State #1 well in Pierce County, Washington. The vitrinite-depth profile is unusual in that (Fig. 3) there is a sudden increase of about 0.3% R_o in reflectance at a depth of about 2200 m (7200 ft) and near-surface values of reflectance are relatively high, with values greater than 0.45% R_o. The slope of the %R_o data versus depth is relatively low, indicating a relatively low geothermal gradient. The "jumps" in %R_o near the surface and at 2200 m depth can be explained by invoking episodes of uplift and erosion, but inordinately large amounts (up to 5000 m) of missing section are needed at both levels because of the apparently low geothermal gradients. Initial modeling with a one dimensional thermal conduction code that does not account for fluid flow revealed that the %Ro profile observed in the Phillips State #1 well, Pierce Co. Washington, could not be satisfactorily simulated with a 1-D conduction model. This is a fundamental problem for the Pacific Northwest area, since the Phillips State #1 vitrinite profile is typical. Recent modeling by Dr. C.Y. Wang - University of California, Berkeley,

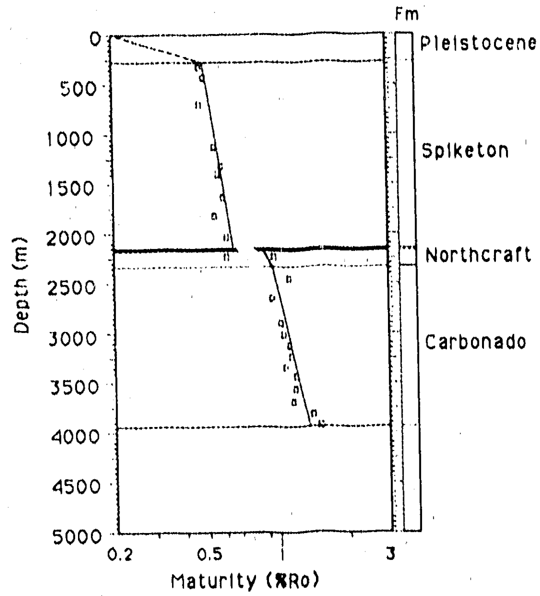

Figure 3. Vitrinite reflectance profile for the Phillips State #1 well, Pierce Co., WA

with a finite element code that incorporates coupled fluid flow and heat conduction - suggests that sudden release of pressure from overpressured argillaceous units lying below rapidly deposited sandy units may allow a sudden, temporary, periodic release of warm fluids into the sediments above, thereby affecting the %Ro values but not the local gradient of %Ro with depth. This preliminary work is being refined to more closely approximate the conditions in the Phillips State #1 well.

We have been using the PYROL code to calculate overpressures developed by the combined effects of sediment compaction and hydrocarbon generation and cracking in the Uinta Basin, Utah. Overpressures have been measured in the Brotherson 1-11B4 well below depths of about 2800 m, continuing to increase to depths of about 3500 m, and leveling off below that. A paradox is that geologic and thermal indicator data suggest that the basin has been uplifted by 1-2 km within the past 10 m.y. and that the sources of overpressuring should have been shut off during that time, allowing the overpressures to dissipate. Our modeling (Fig. 4) suggests that very low permeabilities are needed to account for the overpressures and that it is easier to maintain the observed excess pressure if uplift begins 3 Ma instead of 10 Ma. In our model, the pore pressure reaches a point at which hydrofracturing occurs (which we assume to be when pore pressure reaches 0.8 lithostatic) at about 44 Ma (t = 14 m.y.), during the peak rate of hydrocarbon generation.

FUTURE WORK

We have obtained, from V. Nuccio of the USGS, 20 coal samples from the San Juan Basin that all contain the same original organic matter but range in maturity from 0.4 $\%R_o$ to 1.3 $\%R_o$. These should be excellent samples to carry out a series of pyrolysis experiments for determination of the kinetic parameters for Type III kerogen. The results will be compared to other data, such as that from the Py-TQMS experiments mentioned above, to gain a better understanding of thevariability of cracking behavior in organic matter of different types and richness.

We will carry out sealed bomb pyrolysis experiments on n-hexadecane to validate the results of the free-radical kinetic calculations concerning the effects of pressure on cracking. We will look at cracking rates as a function of pressure in the temperature range of 300-375°C, which has been determined by the calculations to be the critical range to see the effect.

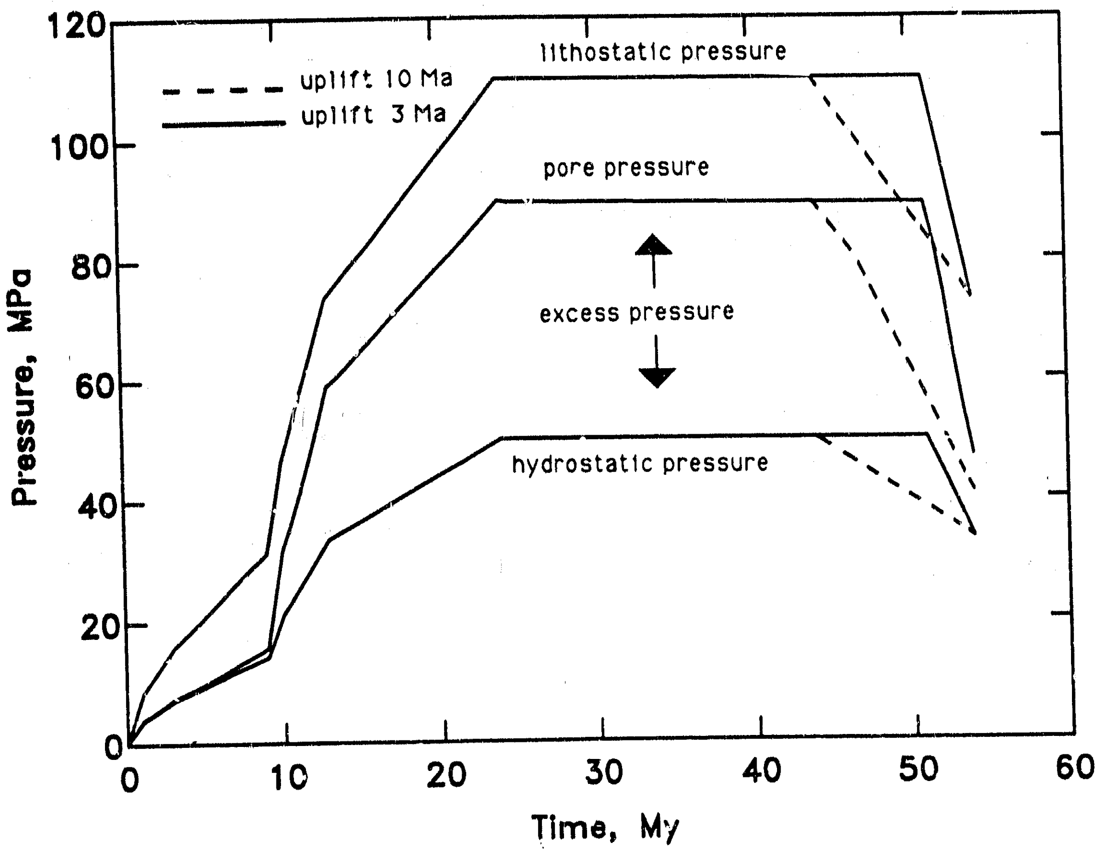

Figure 4. Plot of calculated pressure vs. time for the Brotherson 1-11B4 well, 3400 m depth, Uinta Basin. Note that excess pore pressure at present (right side of plot) is lower when uplift occurs at 10 Ma.

The finite-element code of C.Y. Wang will be used try investigate the role that fluid flow might play in development of the anomalous vitrinite-depth profiles observed in the Pacific Northwest. We also intend to use the code, at least in the 1-D mode, to evaluate the importance of fluid flow in other settings, such as in deep sediment of the Louisiana onshore Gulf Coast.

The final goal of the project is to couple the best available chemical kinetic cracking model with our best estimate of the thermal history for areas like the Pacific Northwest and the Louisiana Gulf Coast to make quantitative assessments of potential deep gas reserves in these areas. Work in both of these regions will be coordinated with ongoing complementary sedimentary basin assessment work being carried out by the USGS.

*This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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Terrestrial Gas Hydrate Occurrences

CONTRACT INFORMATION

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METC Project Manager	Rodney D. Malone
Period of Performance	October 1, 1983 to September 30, 1990
Schedule and Milestones	

FY91 Program Schedule

	O	N	D	J	F	M	A	M	J	J	A	S
Seismic Mapping	----	----	----	----	----	----	----	----	----			
Log Characterization	----	----	----	----	----	----	----	----	----	----	----	----
Walakpa Studies				----	----	----	----	----	----	----	----	----

OBJECTIVES

The primary objective of the DOE-funded USGS Gas Hydrate Program is to assess the production characteristics and economic potential of gas hydrates in northern Alaska. The objectives of this project for FY-1991 will include the following: (1) Map the gas-hydrate/free-gas occurrences in the Prudhoe Bay-Kuparuk River area with newly acquired industry seismic data; (2) Characterize and quantify the well-log characteristics of gas hydrates; (3) Characterize the gas hydrate occurrences in the Walakpa Gas Field in northern Alaska.

BACKGROUND INFORMATION

Sediments of the Arctic region may contain enormous quantities of natural gas in the form of gas hydrates, which are crystalline substances composed of water and mostly methane gas. These ice-like substances are generally found in two distinct environments: (1) offshore in sediments of outer continental margins and (2) nearshore and onshore in areas associated with the occurrence of permafrost.

Cold surface temperatures at high latitudes on Earth are conducive to the development of onshore permafrost and gas hydrate in the subsurface. Gas hydrates are known to be present in the western Siberian platform (Makogon and others, 1972) and are believed to occur in other permafrost areas of northern U.S.S.R., including the Timan-Pechora province, the eastern Siberian craton, and the northeastern Siberian and Kamchatka areas (Cherskiy and others, 1985). Permafrost-associated gas hydrates are also present in the North American Arctic. Well-log responses, attributed to the presence of gas hydrates, have been obtained in about a fifth of the wells drilled in the Mackenzie Delta, and in the Arctic Islands over half of the wells are inferred to contain gas hydrates (Bily and Dick, 1974; Judge, 1988). Direct evidence for gas hydrates on the North Slope of Alaska comes from a core-test, and indirect evidence comes from drilling and open-hole industry well logs which suggest the presence of numerous gas hydrate layers in the area of the Prudhoe Bay and Kuparuk River oil fields (Collett, 1983; Collett and others, 1988). The combined information from Arctic gas-hydrate studies shows that in permafrost regions, gas hydrates may exist at subsurface depths ranging from ≈130 to ≈2,000 m.

Because large quantities of gas hydrates are widespread in permafrost regions they may be a potential energy resource. Estimates of the amount of gas within continental gas hydrates range from 1.4×10^{13} to 3.4×10^{16} cubic meters (5.0×10^{2} to 1.2×10^{6} trillion cubic feet) (adapted from Potential Gas Committee, 1981). Gas hydrates also represent a significant drilling and engineering hazard. Soviet, Canadian, and American researchers have described numerous problems associated with gas hydrates, including blowouts and casing failures.

PROJECT DESCRIPTION

Over the last seven years the DOE-funded USGS Gas Hydrate Program has focused on assessing the resource potential of the in-situ gas hydrates on the North Slope of Alaska. This assessment has resulted in the discovery of an estimated ≈40 tcf of gas trapped as gas hydrates. Recently-completed industry seismic surveys have documented the occurrence of a large free-gas accumulation trapped stratigraphically downdip below the gas hydrates in the west end of the Prudhoe Bay Oil Field. The presence of a gas-hydrate/free-gas contact within the Prudhoe area is analogous to the Messoyakha gas-hydrate/free-gas accumulation in western Siberia from which ≈70 bcf of gas has been produced from hydrates alone. The geologic similarities between these two accumulations are being studied and contrasted. In a recently completed development proposal for the Walakpa Gas Field (located ≈200 miles northwest of Prudhoe Bay) the North Slope Borough reported that the up-dip extension of the Walakpa gas sands may lie within the zone of gas hydrate stability, a conclusion that our studies support. Thermal studies completed by the Borough suggest that the total areal distribution of the potential Walakpa gas hydrate accumulation may be more then 120 square miles. Future research will include the geologic assessment of the potential Walakpa gas hydrate occurrences.

Other ongoing gas-hydrate-related studies in the USGS have focused on the (1) potential geologic hazards of Arctic gas hydrates and (2) the relation between atmospheric methane, a green-house gas, and destabilized in-situ gas hydrates. United States, Canadian, and Soviet researchers have described numerous drilling and production problems attributed to the presence of gas hydrates, including uncontrolled gas releases during drilling, collapsed casings, and gas leakage to the surface. We have documented in several reports geologic problems attributed to the presence of gas hydrates. It is likely that as exploration and development activity moves further offshore into deeper water and to higher latitudes in the Arctic, the frequency of gas hydrate-related problems will increase. Analysis of gases trapped in ice cores indicates that contemporary atmospheric methane concentrations and their rate of increase are unprecedented over the last 160,000 years. Numerous researchers have suggested that destabilized gas hydrates may be contributing to this buildup in atmospheric methane. One of the areas of greatest concern is the thermally unstable continental shelf of the Arctic Ocean. Since little is known about the geology of the Arctic Shelf, our onshore Alaska gas hydrate studies are being used to develop geologic analogs for potential Arctic Shelf gas hydrate occurrences.

RESULTS

To obtain the stated objectives, all available geologic data from the North Slope have been studied including well logs, core data, drill cuttings, drilling reports, and seismic records. For this study four-hundred and forty-five wells were examined for potential gas-hydrate occurrences. Most of the wells are from the Prudhoe Bay--Kuparuk River area; however, all wells from NPRA and most of the exploratory wells to the south and east of Prudhoe Bay have been reviewed. This analysis of all available data sources revealed that gas hydrates occur in 50 of the surveyed wells, all from the Prudhoe Bay-Kuparuk River area.

In the Prudhoe Bay-Kuparuk River area all of the well-log inferred gas hydrates occur below the regional Eocene unconformity and within a 450 to 600 m thick nonmarine to marine sequence of the Sagavanirktok Formation. The gas hydrates occur in six laterally continuous sandstone and conglomerate units and are geographically restricted to the east end of the Kuparuk River Unit and the west end of the

Prudhoe Bay Unit (figures 1 and 2). The gas hydrates occur within relatively porous, discrete rock units. Many wells have multiple gas-hydrate bearing units, with individual occurrences ranging from 3 to 31 meters thick. The six, laterally continuous, discrete gas-hydrate bearing rock units have each been assigned a reference letter (Units A through F), with Unit A being stratigraphically the deepest (figures 1 and 2).

Recently completed three-dimensional seismic surveys have documented the occurrence of a gas-hydrate/free-gas contact at the base of the methane-hydrate stability field in the west end of the Prudhoe Bay Oil Field (public presentation, C.G. Guderjahn, British Petroleum Exploration Inc., Anchorage, Alaska). Open-hole logs from wells in the west end of the Prudhoe Bay field also indicate the presence of a large free-gas accumulation trapped stratigraphically downdip below the log inferred gas hydrates (figures 1 and 2). These well-log delineated free-gas deposits are reservoired within four of the sandstone and conglomerate units that are inferred to contain gas hydrates (Units A, B, C, and D).

Previous estimates of the gas volume that may be attributed to gas hydrates on the North Slope range from 3.1 x 10^{11} to 7,100.0 x 10^{11} m^3 (approximately 11 to 25,000 trillion ft^3 of gas) (Potential Gas Agency, 1981). The broad range of these estimates demonstrates a general lack of knowledge pertaining to actual gas-hydrate occurrence and distribution; however, estimates of this magnitude are of interest especially when compared with the identified North America resource of conventional natural gas of only 142 x 10^{11} m^3.

Most of the published estimates of gas volumes from hydrates have of necessity been made by broad extrapolation of only general knowledge of local geologic conditions that control the distribution and volume of in-situ gas hydrates. Gas volumes that may be attributed to gas hydrates in a permafrost setting are dependent on five reservoir properties: (1) areal extent of the gas-hydrate occurrences, (2) reservoir thickness, (3) porosity, (4) hydrate number, and (5) the degree of gas-hydrate saturation. The total mapped area of all six gas-hydrate occurrences (Units A through F) is about 1,643 km^2, with the areal extent of the individual units ranging from 3 to 404 km^2. The thickness of the gas-hydrate occurrences in Units A through F are highly variable. The thickest gas-hydrate occurrences are those of Unit A, with an average thickness of $\approx$17 m. The thinnest gas-hydrate sequence is that of Unit E, with an average thickness of $\approx$11 m. In our resource estimate, only average values of thickness are used. The calculated porosities of the gas-hydrate reservoir rocks range from 37 to 42 %, and average approximately 39%. The hydrate number can be visualized as a factor describing how much of the clathrate-cage-structure is filled with gas. It is known that one cubic meter of methane hydrate with a hydrate number of 6.325 yields 164 cubic meters of methane (at STP), and a cubic meter of methane hydrate with a hydrate

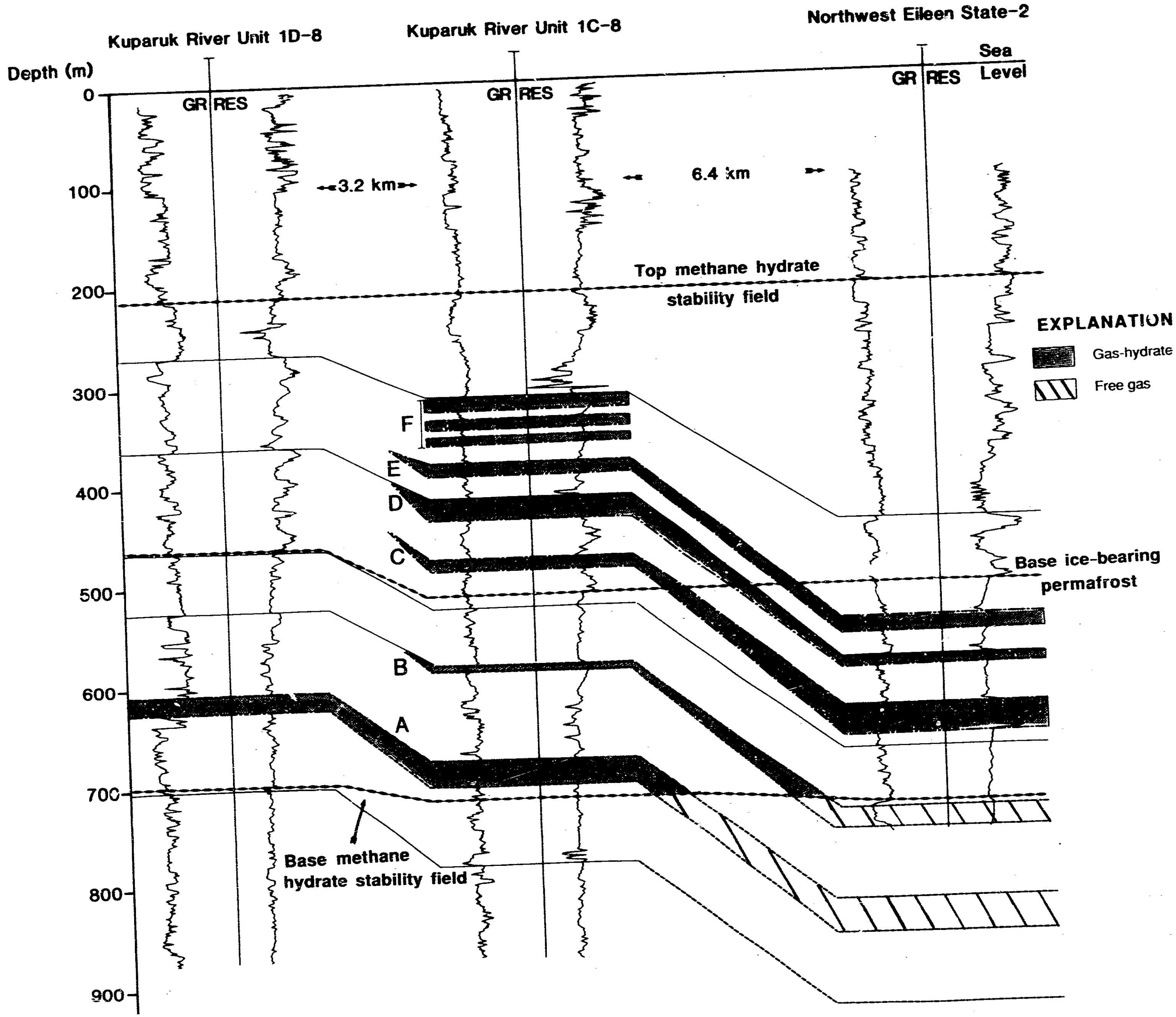

Figure 1. Geologic cross-section showing the lateral and vertical extent of gas hydrates and underlying free-gas occurrences.

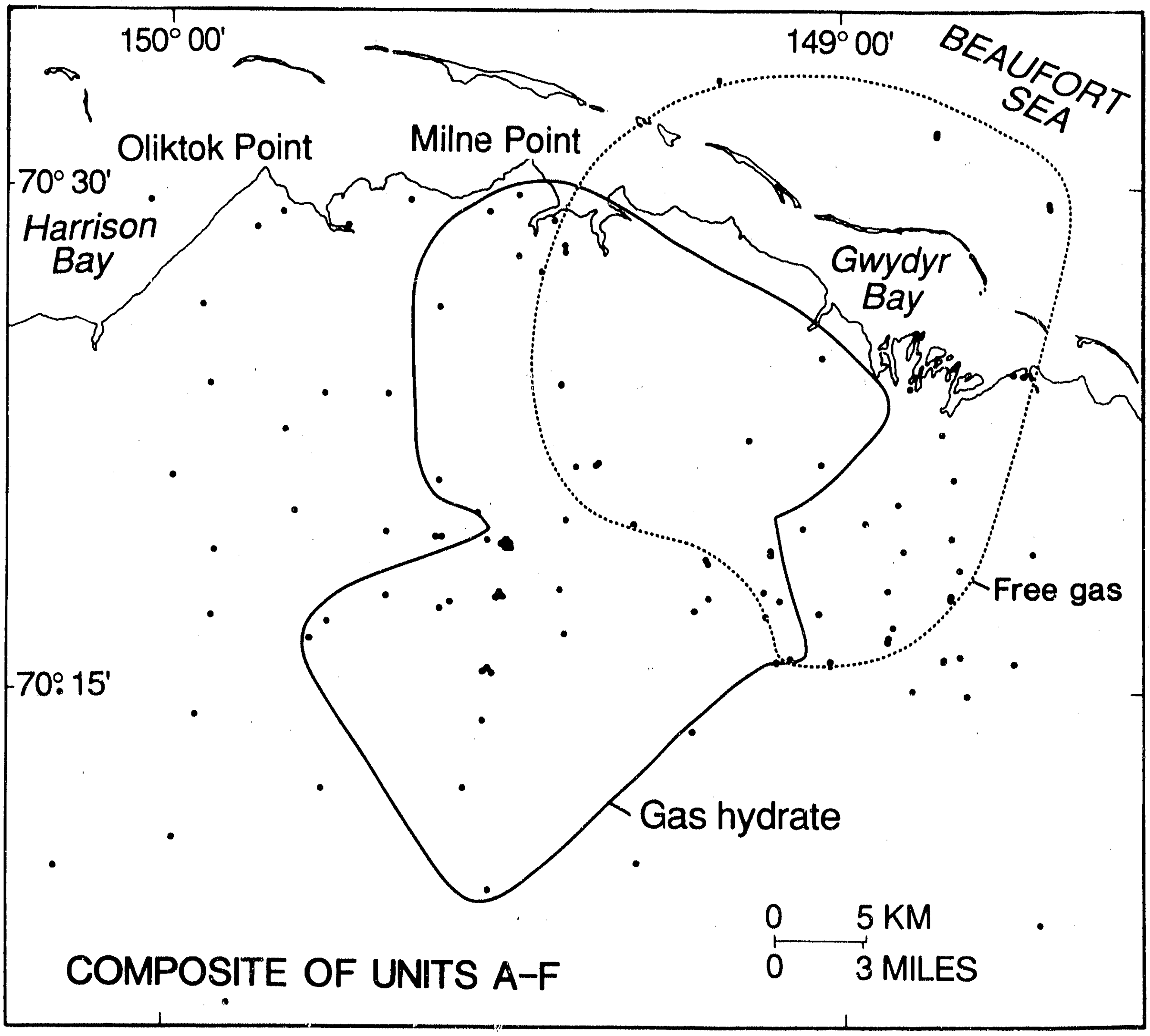

Figure 2. A composite map depicting the geographic distribution of the well-log inferred gas hydrates in the Prudhoe Bay-Kuparuk River area.

number of 7.475 yields 139 cubic meters of methane (at STP).

For each gas-hydrate bearing reservoir, we have calculated the areal extent, average stratigraphic thickness, average porosity, total volume of reservoir porosity, and the average degree of gas-hydrate saturation. The theoretical minimum ($n = 6.325$) and maximum ($n = 7.475$) hydrate numbers have been used to estimate the volume of gas that may be attributed to the identified gas hydrates. These calculations indicate that the potential volume of gas within the identified gas hydrates of the North Slope is approximately 1.0×10^{12} to 1.2×10^{12} m^3 (at STP) [approximately 37 to 44 tcf of gas]. The volume of gas estimated to be present as gas hydrates is about twice the amount of recoverable natural gas (estimated at approximately 8.0×10^{11} m^3) in the Prudhoe Bay field.

Our North Slope gas-hydrate resource estimate must be considered to be relatively conservative because most of the North Slope is sparsely drilled. Outside of the Prudhoe Bay and Kuparuk River development units, drilling density is less than one well for every 500 km^2. Our resource evaluation considers only the well-log delineated gas hydrates which cover an area of only $\approx$400 km^2. Regional geologic information and seismic data suggest that large areas of the North Slope are underlain by relatively good reservoir rocks within the zone of gas-hydrate stability. Because of the low well density of this region, this resource estimate should be considered a minimum value.

Relatively little is known about the history of gas-hydrate formation on the North Slope. However, recent geologic and geochemical studies from the Prudhoe Bay-Kuparuk River area have provided new insight into the geologic parameters controlling the distribution of gas hydrates. As shown in figure 3, most of the gas hydrates and shallow heavy oils occur either up-dip from or near the Eileen fault zone. This fault zone may have acted as a conduit for free-gas and oil migration from deeper hydrocarbon accumulations. Geochemical analyses of drill-cuttings collected from seven industry development wells drilled in the Prudhoe Bay and Kuparuk River oil fields have been used to characterize the composition and source of the hydrocarbon gas within the interval of gas-hydrate stability (Collett and others, 1990). These analyses suggest that methane is the principal hydrocarbon gas in the near-surface (0-1,500m) strata of the North Slope. Stable methane carbon isotopic analyses of gaseous drill-cuttings from several gas-hydrate-bearing rock units yielded carbon isotopic values averaging approximately -49 permil, thus, indicating that the methane within the inferred gas-hydrate occurrences is from mixed sources, microbial and thermogenic. Vitrinite reflectance (R_o) measurements of about 0.4 percent show that the gas-hydrate-bearing rocks have never been subjected to temperatures within the thermogenic window. Thus, the thermogenic gas must have migrated from greater depths.

As noted, a -49 permil stable methane carbon isotopic composition suggests that the gas

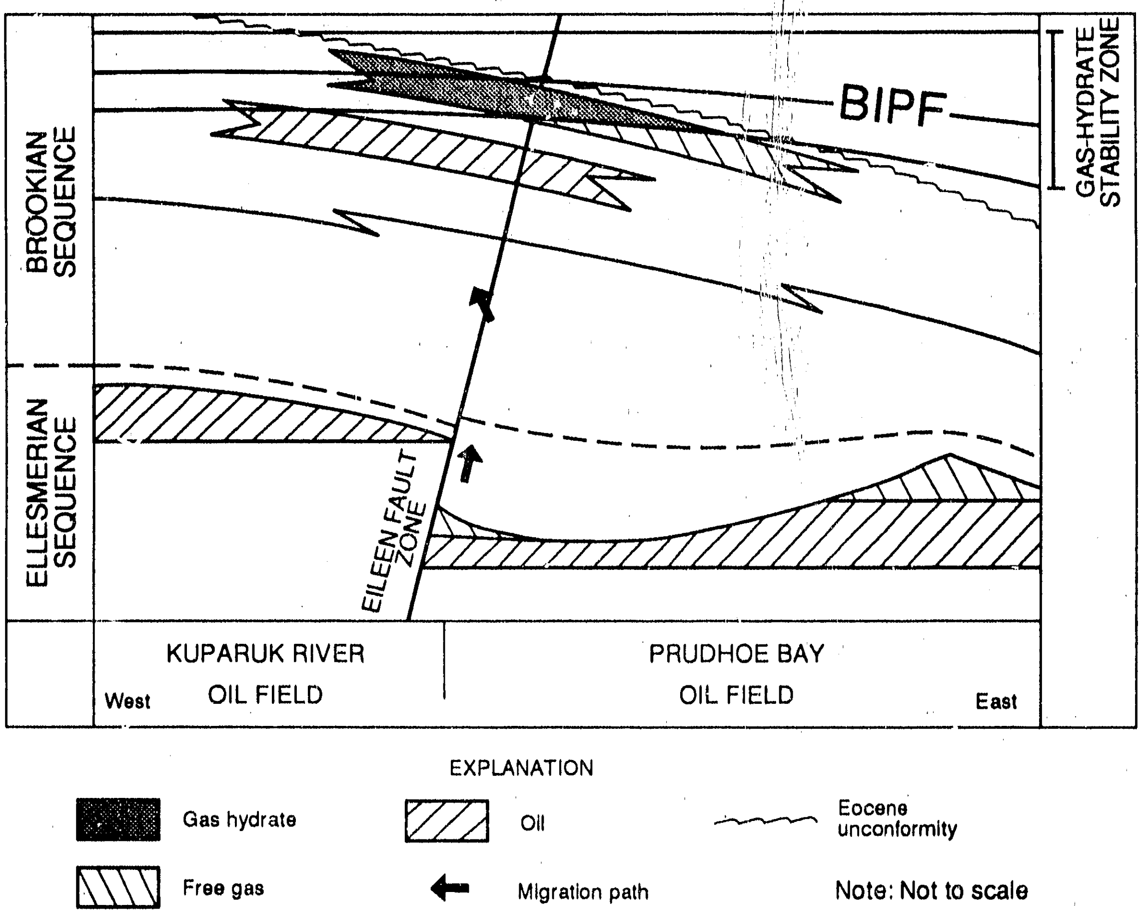

Figure 3. Schematic west to east cross-section through the Prudhoe Bay-Kuparuk River area illustrating possible gas migration paths and spatial relations between gas hydrates, free-gas, oil, Eileen fault zone, base of ice-bearing permafrost (BIPF), and gas-hydrate stability field (adapted from Carman and Hardwick, 1983).

hydrates contain a mixture of thermogenic and microbially sourced gas. By comparing the methane carbon isotopic composition of this apparent gas mixture to the isotopic composition of the Prudhoe Bay gas cap it is possible to calculate the relative volume of thermogenic versus microbially sourced gas within the hydrate stability field. The methane carbon isotopic analysis of the Prudhoe Bay gas cap, considered to be a source for some of the gas within the hydrates, yields an average value of approximately -39 permil (written communication, M.C. Davidson, BP Exploration, Anchorage, Alaska). The microbially sourced methane component likely had an original methane isotopic composition ranging from -60 to -70 permil. Because the mixing of two gases results in a linear and proportional change in isotopic composition, it is estimated that about 50 to 70 percent of the methane within the hydrate stability field has migrated from the Prudhoe Bay gas cap.

To describe the history of gas-hydrate formation, we have adapted a generalized cross section (figure 3) from Carman and Hardwick (1983). As gas moved up the Eileen fault zone and encountered relatively porous and permeable northeast-dipping sandstone units, some of the gas may have been rechanneled up-dip along these beds. The up-dip migrating gas may have collected in structural or stratigraphic traps where subsequent temperature changes deepened the permafrost sequence and converted the trapped gas into gas hydrate. Conversely, the up-dip migrating gas may have converted to gas hydrate upon entering the pressure-temperature regime of gas-hydrate stability, thus forming its own trap. Because so little is known about the history of temperatures on the North Slope either of these scenarios is plausible.

FUTURE WORK

Future activities will focus on the assessment of the production characteristics and economic potential of the gas hydrates in the Prudhoe Bay-Kuparuk River area and if possible, participate in the gas hydrate resource assessment of the Walakpa Gas Field. Other gas hydrate research activities will includ an onshore (near-surface) geochemical sampling program and a gas hydrate mapping study using newly acquired industry seismic data from the Prudhoe Bay-Kuparuk River area.

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Study of Hydrate Dissociation by Methanol and Glycol Injection

CONTRACT INFORMATION

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Contractor Project Manager	Ghanshyam D. Sharma
Principal Investigators	Ghanshyam D. Sharma Vidyadhar A. Kamath
METC Project Manager	Rodney D. Malone
Period of Performance	October 1, 1989 to September 30, 1990

Schedules and Milestones

FY90 Progra

	O	N	D	J	F	M	A	M	J	J	A	S	O
Methanol Experiments													
Data Analysis													
Glycol Experiments													
Data Analysis and Correlation													

OBJECTIVES

The research undertaken in this project addresses the evaluation of various methods such as depressurization, hot water, brine, methanol, glycol and steam injection for production of natural gas from Arctic natural gas hydrate resources. The major project objectives include:

- measurement of permeability changes during formation of dissociation of hydrates in porous media.
- gathering of experimental data on hydrate dissociation for various

processes and understanding dissociation kinetics.

- development of numerical models (finite difference and finite element) to model hydrate dissociation in porous media.
- study of hydrate dissociation under drilling conditions to provide guidelines for safer drilling.

In addition, an experimental study of hydrate formation in the presence of Alaskan North Slope crudes and its effect on crude properties was undertaken to understand the inter-relationship between gas hydrate, heavy oil, and/or tar sand resources.

The objectives of the experimental work on hydrate dissociation during methanol and glycol injection methods are as follows:

- to determine the characteristics of hydrate dissociation process during these methods.
- to determine the effect of inhibitor injection rate and inhibitor concentration on hydrate dissociation rate.
- to develop correlations for hydrate dissociation rate based on experimental results.

BACKGROUND INFORMATION

Due to widespread existence of gas hydrates in deep sub-oceanic sediments and arctic onshore and offshore areas as well as due to very high concentration of natural gas in hydrate (170-180 SCF/ft^3 hydrates), they represent long-term future resource of natural gas. Production of natural gas from hydrate resources in U.S. has not been commercialized yet. The only commercial production of a hydrate reserve has been in the Messoyakha field in the U.S.S.R. (Makogon, 1987), where the gas hydrate overlies the gas reserves.

Since hydrates are relatively immobile and impermeable, they need to be dissociated into gas and water to produce natural gas from hydrate reservoirs. Depressurization, thermal techniques such as steam, hot water and brine injection and in-situ combustion or injection of hydrate inhibitors such as glycols and methanols are some of the techniques which could be used for production of natural gas from hydrate reservoirs. Fracturing, thermal stimulation followed by depressurization could be used to increase productivity. The applicability of the technique will be governed by the economics, the type of hydrate reservoir (all hydrates, hydrates + free gas, hydrates + excess ice, hydrates + excess water, and hydrates + oil), the form in which hydrates exist in the reservoir (massive, layered, nodular, and disseminated) and the reservoir properties such as permeability, porosity, hydrate saturation, etc.

The quantity of gas that can be produced from hydrate reservoirs will depend upon the hydrate dissociation kinetics under each of the producing mechanisms. The experimental data on hydrate dissociation kinetics will be useful in evaluating the technical feasibility of each of these processes.

PROJECT DESCRIPTION

This project entitled, "Development of Alaskan Gas Hydrate Resources," began under the joint agreement between the U.S. Department of Energy and the State of Alaska in on October 1, 1986. The project completion date is March 31, 1991. The work performed during the past year (October 1, 1989 - September 30, 1990) is described in this paper, and the major accomplishments during the previous years (October 1, 1986 - September 30, 1989) are summarized below:

Summary of Past Accomplishments

- Task 1 (gathering of data and information relevant to gas hydrates in Arctic Alaskan North Slope) has been completed, and a review report along with a list of bibliography has been compiled.

- Task 2 (review of gas hydrate literature and the state-of-the-art technology) has been completed, and a complete review report on gas hydrates has been prepared.
- Nomograms for determination of potentially stable gas hydrate zones in Arctic onshore and offshore environments have been developed..
- Analytical model for hot brine, water and steam stimulation techniques for recovery of natural gas from hydrates has been developed and used to evaluate these methods.
- A 2-D, r-z, finite difference model to predict hydrate dissociation during drilling through hydrate zones has been developed. This model has been converted to a user friendly, menu-driven, interactive computer program. This model has been coupled with wellbore hydraulics model to predict degree of dissociation of hydrates during drilling through hydrate zones. Sensitivity analysis has been performed to study effect of various drilling parameters on hydrate dissociation. A nomogram for estimating drilling fluid parameters (mud density, mud temperature, mud circulation rate) for controlling gas influx into wellbore from hydrate dissociation has been developed. Based on these results, guidelines for safer hydrate drilling procedures have been established.
- Experimental setup has been constructed and used to measure phase behavior of hydrate formation in presence of Alaskan North Slope crude oils such as West Sak crude (heavy oil) and Prudhoe Bay crude (light oil). Experimental measurements have been used to determine the effect of hydrate formation on crude oil properties. These results support the well log evidence of presence of hydrates along with heavy oils and tar sands in the shallower section of the southwest portion of the Kuparuk River Unit and suggest that the properties of these crudes might have been altered due to formation of hydrates during up-dip migration of hydrocarbons to the west.
- Experiments on measurement of effective permeability changes of hydrate containing unconsolidated cores have been completed. Based on the results, a correlation between effective core permeability reduction factor and hydrate saturation in the core has been developed. Typically, hydrate formation reduces the effective gas permeability of the core by a factor 45 to 110 depending upon the hydrate saturation.
- A series of experiments has been performed to dissociate the laboratory formed hydrate cores by injection of hot water. In these experiments, the effect of water injection rate and pressure on the rate of hydrate dissociation has been studied.
- The methane hydrates in the cores have been dissociated by injection of brine, In these experiments, the effect of brine salinity, brine temperature and brine injection rate on the hydrate dissociation rate has been studied. Based on the experimental results, correlation of hydrate dissociation rate has been developed.
- Hydrates in the cores have been also dissociated by depressurization technique under constant gas production. Effect of gas production rate on hydrate dissociation rate and pressure decline has been studied. The effect of initial hydrate temperature on the hydrate dissociation has also been studied.
- A comprehensive 2-D, r-z, finite element model for hydrate dissociation has been developed. Although the model performance has been tested and validated for several cases such as single phase gas reservoir, 2 phase (gas-water flow), 2 phase flow with heat transfer for which literature data

were available, it has not been used to predict performance for hydrate reservoir.

Experimental Study of Hydrate Dissociation By Methanol and Glycol Injection

In this study, characteristics of methane hydrate dissociation process during injection of methanol and ethylene glycol were investigated. This work is an extension of previous experimental work by Kamath et al. (1989) in which methane hydrate dissociation during brine injection was studied. The experimental set-up used for formation and dissociation of hydrates is same as that used by Kamath et al. (1989).

In each experiment, the first step was to form methane hydrates in the laboratory made cores. The hydrate formation technique used in this study is same as that described by Kamath et al. (1989). Tables 1 and 2 provide the properties of methane hydrate cores used in the study of hydrate dissociation by methanol injection method and ethylene glycol injection method respectively.

In order to study dissociation characteristics of methane hydrates by inhibitor (methanol or ethylene glycol) injection, following procedure was used. Initially, an aqueous solution of desired initial inhibitor concentration was prepared. The initial core holder pressures and temperatures were recorded. The dissociation run was then started by injecting inhibitor solution from the inhibitor reservoir into the core holder at a constant preset injection rate. During the entire dissociation run, pressure in the core holder and inhibitor injection rate were held to a constant value. During the entire dissociation run, the temperature of the bulk inhibitor solution in the core holder, the temperature of hydrates, the gas production, the pressure in the core holder and the level of inhibitor in the inhibitor reservoir were recorded at one minute intervals. By monitoring the inhibitor level in the inhibitor reservoir, the position of dissociating hydrate surface was tracked. The run was stopped when about 80 to 90% of the hydrates were dissociated. The initial and final concentration of inhibitor solution were measured by HP 5880 gas chromatograph. Series of dissociation experiments were conducted to study effect of inhibitor concentration and inhibitor injection rate.

As the hydrate dissociation proceeded in each run, the concentration of the inhibitor in the solution decreased continuously due to generation of water from hydrate dissociation. Moreover, the temperature of the inhibitor solution also decreased continuously since no temperature control was used. The driving force for the dissociation of hydrates is the difference between the temperature of inhibitor solution in contact with hydrates (T_f) and the temperature of the dissociating hydrates at the Interface (T_I). For 0% concentration, temperature of dissociating hydrates (T_I^o) was obtained from the equilibrium P-T relationship for methane hydrates and is given by

$$T_I^o = \frac{8533.8}{38.98 - ln(P)} - 273.15 \quad for\ T_I^o \geq 0 \qquad (1)$$

or

$$= \frac{1886.8}{14.717 - ln(P)} - 273.15 \quad for\ T_I^o < 0 \qquad (2)$$

where P is the core holder pressure in kPa and $T_I{}^o$ is in °C. The "Apparent" temperature driving force, (ΔT^o) without taking in to account the effect of inhibition was then obtained from:

$$\Delta T^o = T_f - T_I^o \qquad (3)$$

The "True" temperature driving force, (ΔT) was obtained by incorporating inhibition effect as follows:

$$\Delta T = \Delta T^o + \Delta T_x \qquad (4)$$

where ΔT_x was obtained from equation (5) for methanol injection and equation (6) for ethylene glycol injection.

$$\Delta T_x = 0.3938x + 0.006166x^2 (METHANOL) \quad (5)$$

$$= 0.1721x + 0.004466x^2 (E\,GLYCOL) \quad (6)$$

where ΔT_x is in (°C) and x is wt% inhibitor in solution.

RESULTS

Table 3 provide a summary of experimental conditions during hydrate dissociation by methanol injection. In runs 1 to 4, initial concentration of methanol solution injected was kept same at 30 wt% and methanol injection rate was varied from 7.33 (cc/sec) to 26.67 (cc/sec). In runs 4 to 7, the methanol injection rate was maintained same at 26.67 (cc/sec) and methanol concentration was varied from 10 to 30 wt%. The pressure in the core holder during each run fluctuated within ± 35 kPa.

All dissociation runs (methanol and glycol injection) were unsteady state during which the hydrate dissociation rate decreased continuously with time as illustrated by a typical run in Figure 1. Reasons for the unsteady state behavior are as follows. The concentration of inhibitor in the solution decreased continuously with time as shown in Figure 2 due to dilution of inhibitor from water generated by hydrate dissociation. In addition, the temperature of inhibitor or the temperature difference between inhibitor and hydrates decreased continuously with time as shown in Figure 3 since no temperature control was adopted. Thus, the true temperature driving force, (ΔT) decreased with time in all the runs. Figure 4 shows the effect of methanol injection rate on the cumulative gas produced from hydrate dissociation as a function of time for runs 1-4. In general, the increase in methanol injection rate increased the cumulative gas production since the forced convection effect played role in hydrate dissociation. The same effect is also shown in Figure 5 where hydrate dissociation rate is plotted as a function of apparent temperature driving force ΔT^o. Figure 4, shows the effect of initial methanol concentration on the cumulative gas produced as function of time for fixed injection rate (runs 4-7). Increase in initial concentration results in higher true temperature driving force causing increased rate of hydrate dissociation.

In order to develop a correlation for rate of hydrate dissociation as a function of pressure, methanol solution temperature, methanol concentration, and hydrate-methanol interfacial area, unsteady state data from runs 4-7 were considered. The effect of pressure, temperature of methanol solution and concentration of methanol on hydrate dissociation was accounted by defining the true temperature driving force given in equation 6. The effect of inhibitor-hydrate interfacial area is accounted by defining hydrate dissociation rate as $Q_g/\Phi_H A$ (gmol methane produced per cm^2 hydrates at interface per sec.), where Φ_H is the volume (or area) fraction hydrates in the core. Figure 7 shows the correlation for rate of methane hydrate dissociation by methanol injection which is given by following equation:

$$\frac{Q_g}{\Phi_H A} = 4.557 \times 10^{-7} (\Delta T)^{1.668} \quad (7)$$

where ΔT is true temperature driving force (°C) given by equation (4). The average absolute percentage error in this correlation is 13.9%.

To illustrate the effect of methanol inhibition on the degree of enhancement in the hydrate dissociation rate, which is defined as the ratio of dissociation rate at 0% concentration, (Q_g^o) to dissociation rate at specified methanol concentration, (Q_g) at given ΔT^o (apparent temperature driving force) was plotted versus methanol concentration (see Figure 8). At low ΔT^o values there is stronger effect of methanol inhibition than at high ΔT^o values.

Table 4 provides a summary of experimental conditions during hydrate dissociation by ethylene glycol injection. In runs 1-3 and 7, ethylene glycol injection rate was maintained same as 26.67 cc/sec and initial glycol concentration was varied from 10 to 30 wt%. In runs 3-7, initial glycol concentration was kept same at 30% and injection rate was varied from 6.67 to 26.67 cc/sec. The experimental method, data analysis procedure was same as described earlier.

Figure 9 shows the effect of hydrate dissociation on the dilution of glycol solution. Figure 10 shows the effect of glycol injection rate (forced convection effect) on the cumulative gas produced. Figure 11 shows the effect of glycol concentration on the cumulative gas production. These effects are similar to those described for methanol injection runs. Figure 12 shows the correlation for rate of methane hydrate dissociation by glycol injection which is given by following equation:

$$\frac{Q_g}{\Phi_H A} = 8.606 \times 10^{-8} (\Delta T)^{2.578} \qquad (8)$$

The average absolute percentage error in this correlation is 17.3%. In general, the rate of hydrate dissociation during water, brine, methanol or glycol injection methods can be expressed as:

$$\frac{Q_g}{\Phi_H A} = a\, \Delta T^b \qquad (9)$$

where a and b are constants and ΔT is true temperature driving force. The comparison of constants a and b for various hydrate dissociation methods is provided in Table 5.

The following conclusions have been drawn:

1. In this experimental study, the effect of inhibitors such as methanol and ethylene glycol on the rate of methane hydrate dissociation was investigated. Applications of this work include use of inhibitors for prevention of hydrate formation in natural gas processing and transportation and for production of natural gas from hydrate reservoirs.
2. Experimental results show that the rate of hydrate dissociation is function of concentration of inhibitor, rate of injection of inhibitor, pressure, temperature of inhibitor solution and hydrate-inhibitor interfacial area.
3. The inhibitors are excellent hydrate dissociation stimulants and the use of inhibitor results in significant enhancement in the rate of hydrate dissociation.
4. Based on experimental results, correlations of hydrate dissociation rates for methanol and glycol injection are developed and are consistent with the previous correlations for hydrate dissociation rate for brine and water injection.

FUTURE WORK

- Conduct hydrate dissociation experiments by continuous steam injection technique to study the effect of the steam injection rate and steam temperature.
- Conduct hydrate dissociation experiments by steam soak method to study the effect of steam soak time.
- Continue work on the application of finite element model to study performance of hydrate dissociation under various techniques.
- Study economics of gas hydrate production.

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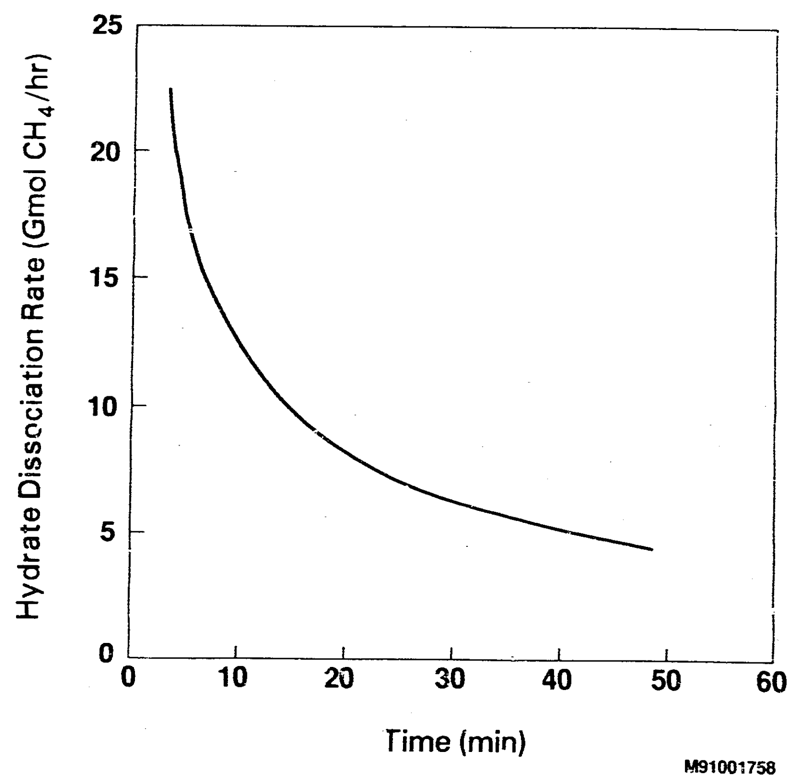

Figure 1. Typical Hydrate Dissociation Run (Methanol)

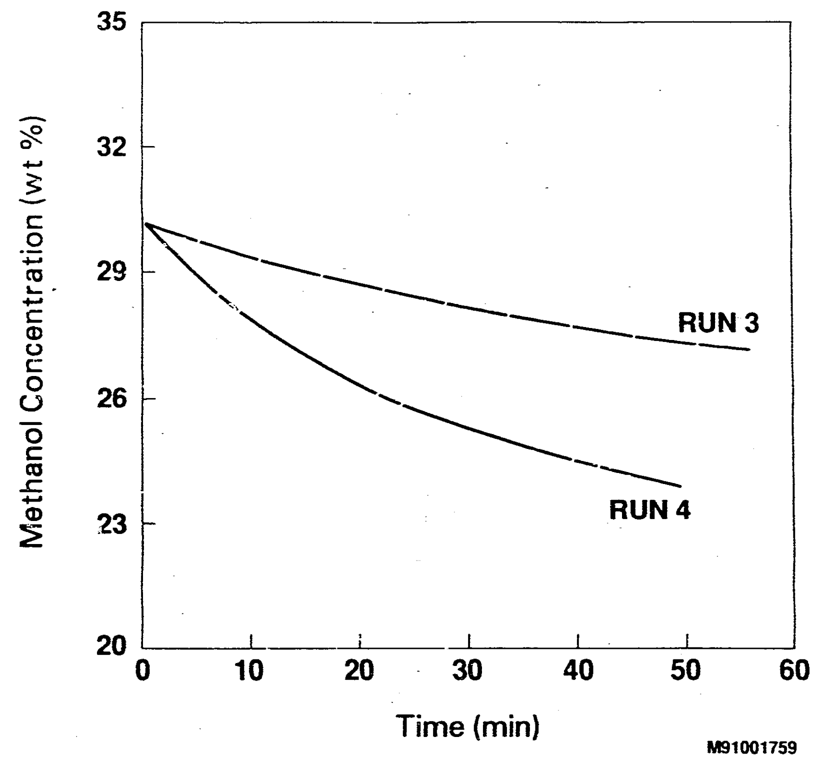

Figure 2. Dilution of Methanol by Hydrate Dissociation

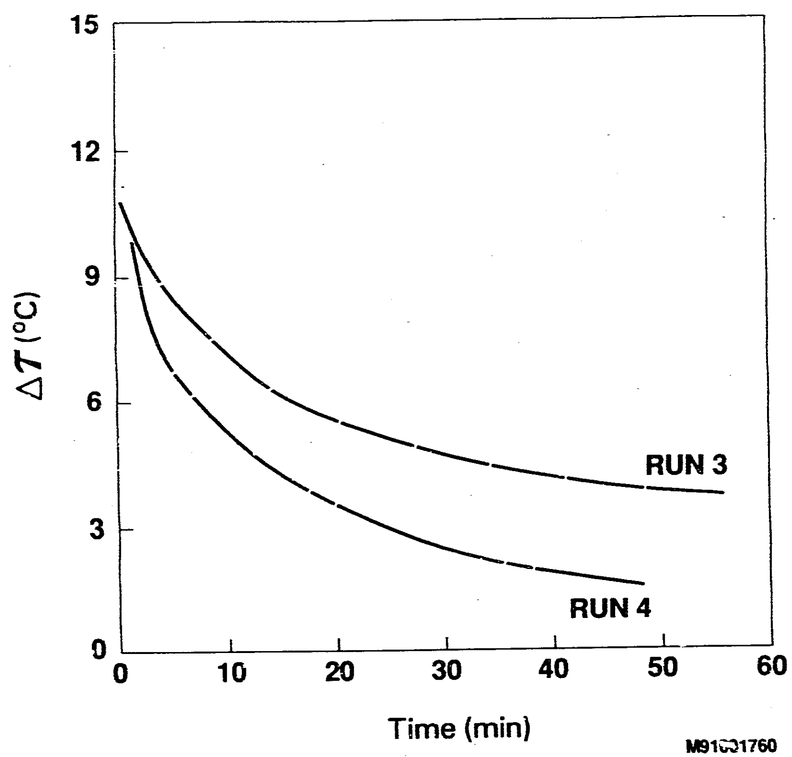

Figure 3. Decrease in Temperature Driving Force

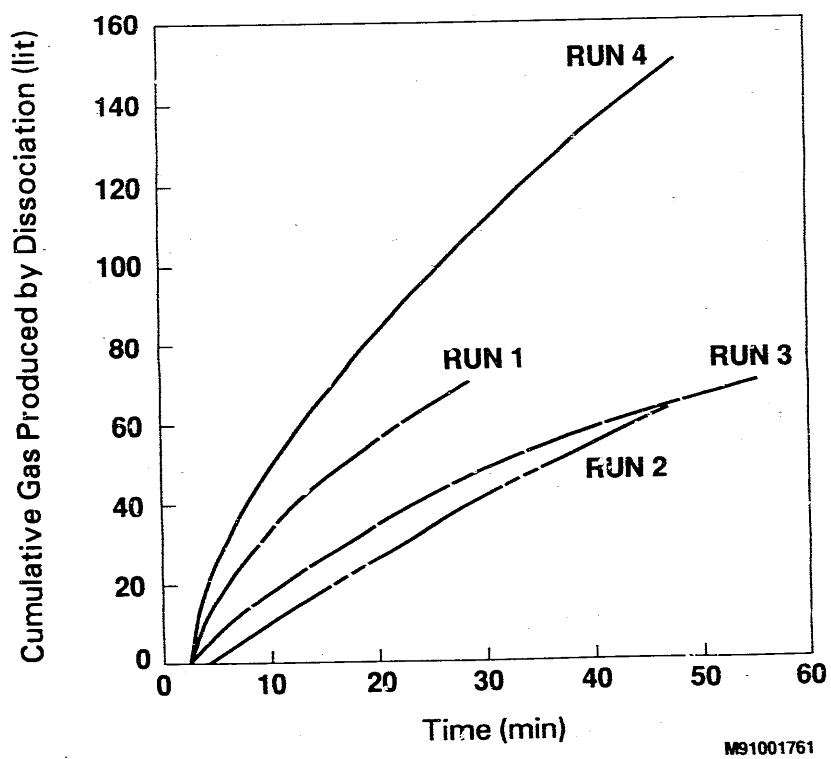

Figure 4. Effect of Methanol Injection Rate on Cumulative Gas Production (30 wt% Methanol)

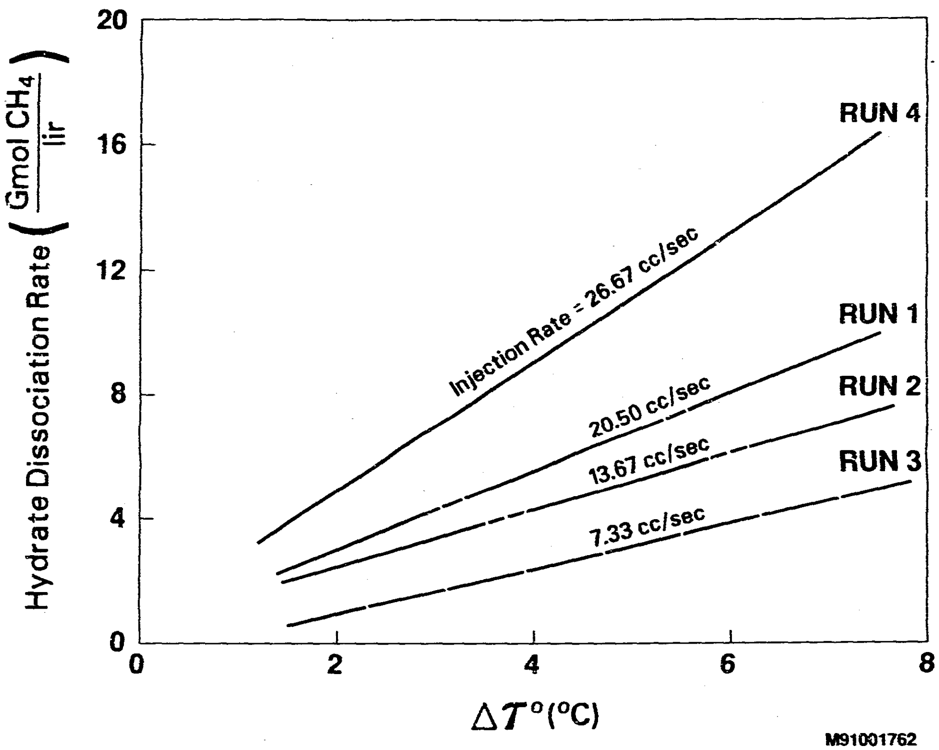

Figure 5. Effect of Methanol Injection Rate on Hydrate Dissociation Rate

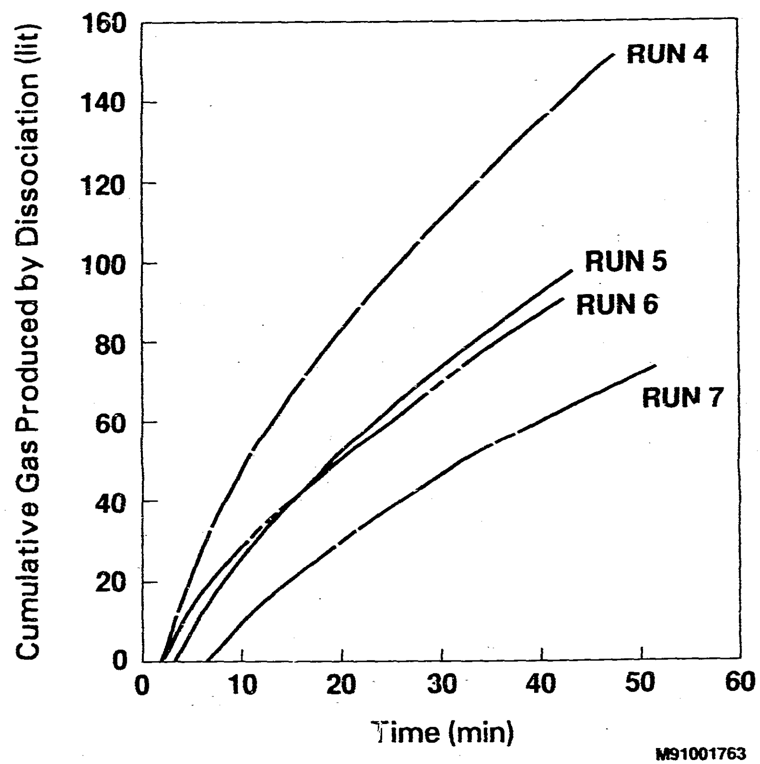

Figure 6. Effect of Methanol Concentration on Cumulative Gas Production (Injection Rate = 26.67 cc/sec)

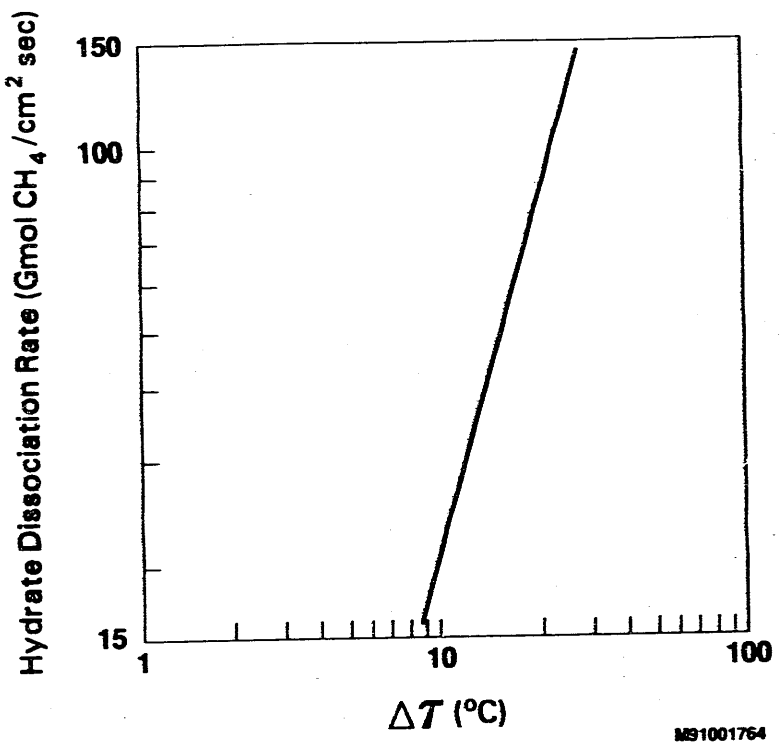

Figure 7. Hydrate Dissociation Correlation (Methanol Injection)

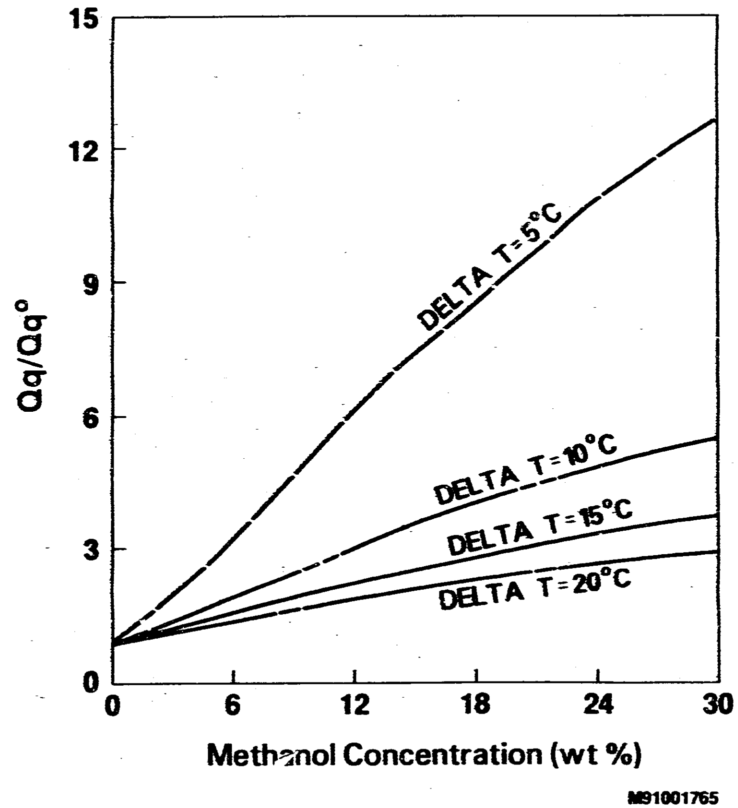

Figure 8. Effect of Methanol Inhibition on the Degree of Enhancement in Hydrate Dissociation Rate

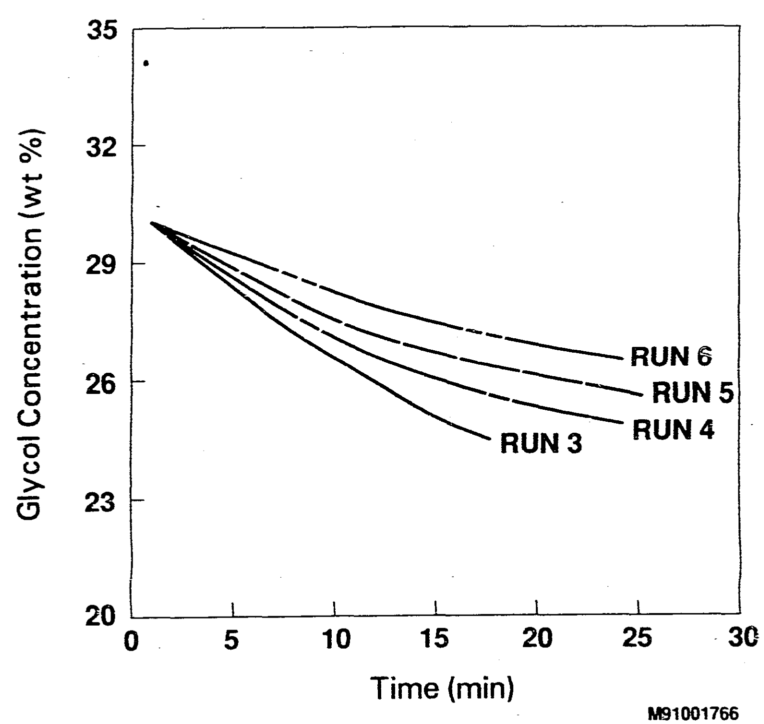

Figure 9. Dilution of Glycol by Hydrate Dissociation

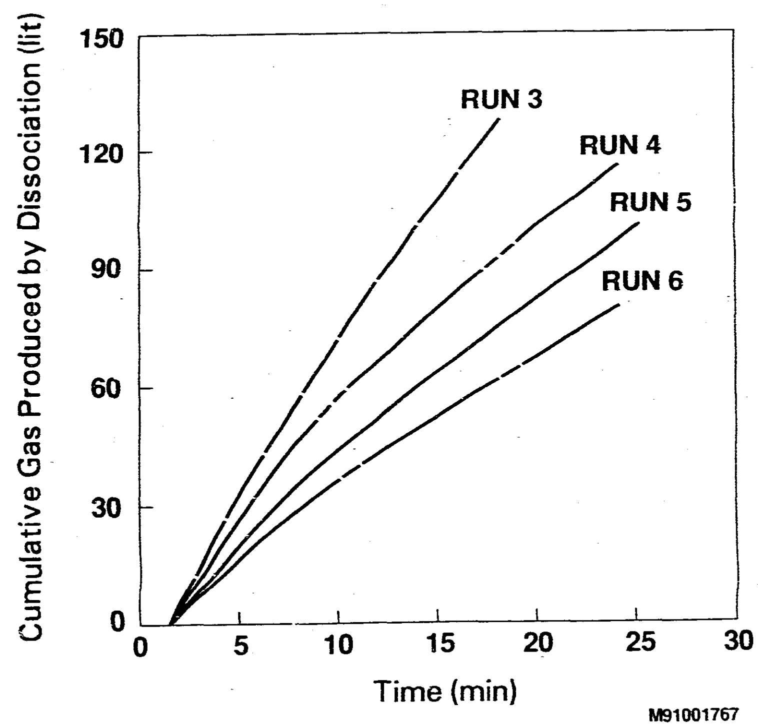

Figure 10. Effect of Glycol Injection Rate on Cumulative Gas Production (30 wt% Glycol)

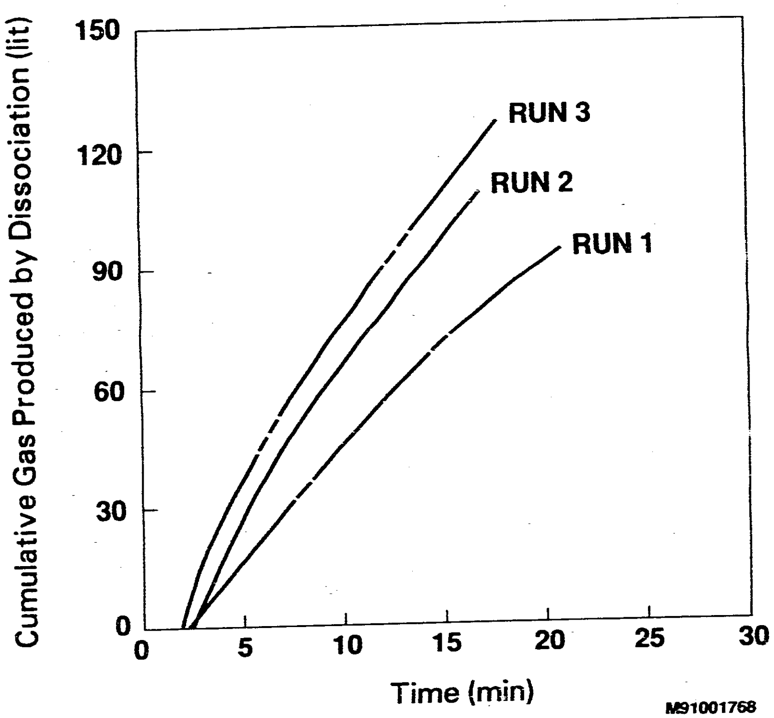

Figure 11. Effect of Glycol Concentration on Cumulative Gas Production (Injection Rate = 26.67 cc/sec)

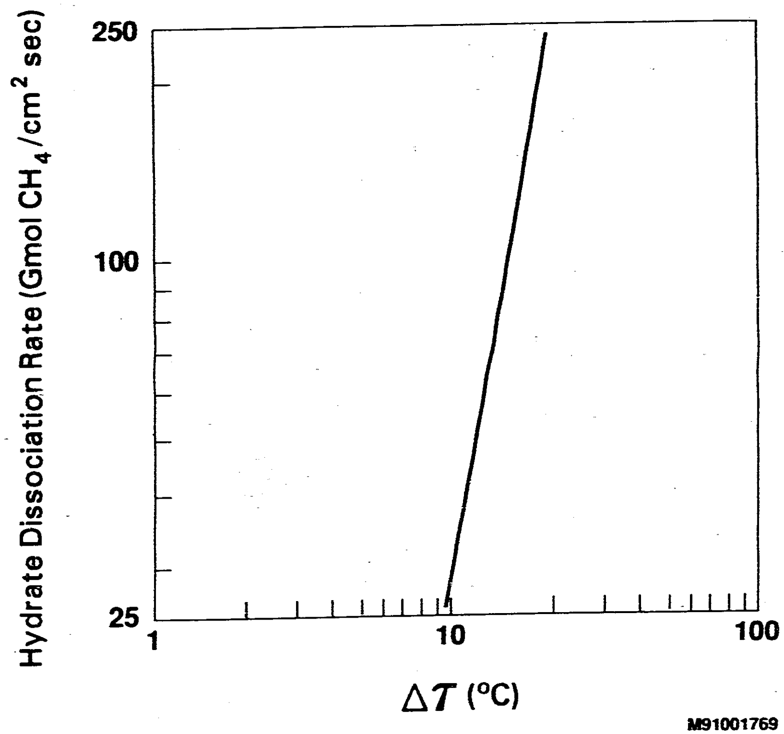

Figure 12. Hydrate Dissociation Correlation (Glycol Injection)

Table 1. Properties of Methane Hydrate Cores Used in the Study of Hydrate Dissociation by Methanol Injection

Run No.	Core Length (cm)	Amount of H_2O in the Core	Initial Core Porosity (%)	Hydrate Formation Period (hr)	Conversion of H_2O to Hydrates (%)	Vol. % Hydrates in the Core
1	21.5	806.0	49.5	46	54.7	32
2	21.5	805.0	49.6	91	68.3	40
3	21.7	805.0	50.1	145	71.2	41
4	21.6	805.0	49.8	113	71.9	42
5	21.7	805.0	50.1	64	69.9	40
6	21.9	830.0	49.0	172	69.3	41
7	20.5	830.0	45.5	244	76.3	48

Table 2. Properties of Methane Hydrate Cores Used in the Study of Hydrate Dissociation by Ethylene Glycol Injection

Run No.	Core Length (cm)	Amount of H_2O in the Core	Initial Core Porosity (%)	Hydrate Formation Period (hr)	Conversion of H_2O to Hydrates (%)	Vol. % Hydrates in the Core
1	21.5	815.0	49.0	150	71.1	42
2	21.7	810.0	49.8	71	70.9	41
3	21.9	825.0	49.3	119	72.1	42
4	21.6	820.0	48.9	72	71.4	42
5	21.5	816.0	48.9	97	73.9	44
6	21.6	814.0	49.3	72	71.3	42
7	21.6	810.0	49.5	172	58.7	34

Table 3. Experimental Conditions for Hydrate Dissociation by Methanol Injection

Run No.	Dissociation Run Time (min)	Methanol Injection Rate (cc/s)	Initial Methanol Concentration (wt %)	Final Methanol Concentration (wt %)	Average Run Pressure (kPa)	Methanol Temp. (°C)
1	29	20.50	30.0	26.7	4412	7.4 - 14.6
2	48	13.67	30.0	26.6	4522	8.1 - 14.8
3	56	7.33	30.0	27.0	4247	9.6 - 17.4
4	49	26.67	30.0	23.9	4747	8.1 - 16.6
5	44	26.67	20.0	17.1	4745	8.6 - 15.3
6	43	26.67	20.0	17.2	4747	9.7 - 16.3
7	53	26.67	10.0	8.9	4693	9.1 - 15.6

Table 4. Experimental Conditions for Hydrate Dissociation by Ethylene Glycol Injection

Run No.	Dissociation Run Time (min)	Glycol Injection Rate (cc/s)	Initial Glycol Concentration (wt %)	Final Glycol Concentration (wt %)	Average Run Pressure (kPa)	Glycol Temp. (°C)
1	22	26.67	10.0	8.6	4757	15.5 - 19.7
2	18	26.67	20.0	16.7	4806	17.8 - 21.7
3	19	26.67	30.0	24.5	4819	17.7 - 23.5
4	25	20.00	30.0	24.8	4771	16.3 - 21.3
5	26	13.67	30.0	25.5	4778	15.4 - 19.7
6	25	6.67	30.0	26.4	4792	14.8 - 18.3
7	28	26.67	30.0	26.6	4854	10.7 - 21.8

Table 5. Constants "a" and "b" in Hydrate Dissociation Correlation (Eq. 9)

Hydrate Type	Injection Fluid	Constant "a"	Constant "b"	% Error	Reference
Propane	Water	4.808×10^{-7}	1.605	5.3	Kamath et al. (1984)
Methane	Water	1.4508×10^{-7}	2.16	13.5	Kamath and Holder (1987)
Methane	Brine	1.353×10^{-7}	2.195	22.0	Kamath et al. (1989)
Methane	Methanol	4.557×10^{-7}	1.668	13.9	This Study
Methane	Glycol	8.606×10^{-8}	2.578	17.3	This Study

Seismic Interpretation of Gas Hydrates in the Blake Ridge Area

CONTRACT INFORMATION

Interagency Agreement	DE-AI21-83MC20422
Contractor	U.S. Geological Survey Reston VA 22092 703-648-6470
Contract Project Manager	Thomas Ahlbrandt
Principal Investigator	William Dillon
METC Project Manager	Rodney Malone
Period of Performance	Feb 23, 1990 to Feb 23, 1991
Schedule and Milestones	

FY90/91 Program Schedule

	M	A	M	J	J	A	S	O	N	D	J	F
Install seis. processing system, Woods Hole	--	--										
Purchase commercial seismic data	--	--										
Subcontract to university researchers	--	--	--	--								
Process commercial seismic data			--	--	--	--	--					
Process 2-channel seismic data			--	--	--	--	--	--	--	--		
Model hydrate effects in seismic profiling					--	--	--					
Interpret processed profiles							--	--	--	--	--	
Digitize and map hydrates									--	--	--	--

OBJECTIVES

The purposes of this project are: (1.) to determine the amount of methane that is bound in gas hydrates in marine sediments, (2.) to understand the distribution of gas hydrates and (3.) to relate the amounts and distribution of hydrate to geological settings and geological/geochemical processes. Previously, seismic profiling data has been used as evidence for gas hydrates in marine sediments. Such data can be used to identify hydrates because a seismic reflection is produced by the base of the layer of gas hydrate that forms just below the sea floor. Although such seismic information is good evidence for the presence of gas hydrates, it tells us nothing about the critical questions of the volume of hydrate and amount of gas present. Determining the volume of gas hydrate and mapping its distribution requires an innovative approach to the use of seismic profiling data.

BACKGROUND INFORMATION

Gas hydrates are ice-like crystalline solids (known as clathrate compounds) that are formed of a lattice of water molecules surrounding a gas molecule. Sea floor sediments of the world oceans, below a few hundred meters of water depth, lie in the pressure/temperature zone of phase stability for gas hydrates. Because of the geothermal gradient, however, the temperature at depths of several hundred to about a thousand meters below the sea floor rises above that at which hydrate is stable. Evidence for the presence of hydrates in the upper several hundreds of meters of the sedimentary section has come both from seismic profiling data and from direct sampling. The sampling suggests that the gas in most naturally-occurring gas hydrates is mainly methane (Kvenvolden, 1988).

Gas hydrates are gas concentrators; in methane hydrates, the gas is concentrated 164 times (Kvenvolden, 1988), so that the relative density of gas in hydrates exceeds its density in the liquid state (Makogon, 1981). Although not well defined, the amount of methane that is trapped in gas hydrates in sea floor sediments probably is enormous. A recent estimate suggests that the amount of methane in hydrates probably exceeds, in its carbon content, that present in all fossil fuel deposits plus the total organic carbon in the atmosphere, terrestrial biota, terrestrial soil detritus and peat, marine biota, and marine dissolved materials; it is exceeded only by dispersed carbon in sediments and rocks (Kvenvolden, 1988). The probably immense amount of such gas encourages research on its availability as an energy resource. Furthermore, methane is a greenhouse gas, and, therefore, estimation of the amount of gas trapped in gas hydrates within sea floor sediments and research on the processes whereby gas can enter and leave this reservoir are critical to analysis of global climate change. The elevated acoustic velocity of gas-hydrates also affects sound propagation in sea floor sediments, which affects sonar transmissions, and so is of concern for defense reasons.

The seismic-profile evidence that has been used to identify hydrates consists of a reflection that approximately parallels the sea floor, and therefore is known as the "bottom simulating reflector" or "BSR" (Dillon and Paull, 1983). The BSR is observed at the depth of the isotherm that defines the phase boundary of gas hydrate at the appropriate pressure. Hydrates exist above, and not below this limit (free gas can exist below). Because the BSR is a geochemical rather than a geological boundary, the reflection from the base of hydrate cementation commonly cuts through reflections from sedimentary strata. In seismic reflection profiles, reflections result from changes in acoustic impedance of adjacent layers, changes that are caused by variations in density or velocity. Hydrates increase the velocity of sediments (pure methane hydrate has a velocity of about 3.3 km/s; Sloan, 1990) and they slightly reduce the density. The BSR identifies the presence of gas hydrate cementation of sediments, but, as it is only a reflection from the base of the cementation, it gives us no idea as to the volume of hydrate. However, another characteristic that we have noted in seismic profiles may allow us to estimate volumes of hydrate cementation. This characteristic is the appearance of blanked spots in seismic records (zones of reduced amplitude of reflections). Apparently the cementation of sediments by gas hydrates suppresses the amplitude of reflections from sedimentary layers, creating a characteristic blanking of portions of the seismic record. Such an hypothesis is supported both by theoretical considerations and examination of seismic profiles from around the world.

This project is being funded as a cooperative effort between the Department of Energy, Morgantown Energy Technology Center and the Department of Interior, Geological Survey, Branch of Atlantic Marine Geology.

PROJECT DESCRIPTION

The primary effort of this project is to map distribution and volumes of gas hydrates by using seismic reflection profiles. For this first year of work, we have selected the Blake Ridge region off North Carolina for our study area (Dillon et al. 1980; Paull and Dillon, 1981). This is a region where gas hydrates were first identified in the deep sea. It is an ideal location to initiate this new approach to hydrate study because it has well-defined and apparently abundant hydrates at a range of water depths, and drilling has been carried out by the Deep Sea Drilling Project to sample and analyze the gas. Furthermore, the U.S. Geological Survey (USGS) has long studied this area, so a network exists of deep-penetration, industry-collected multichannel seismic profiles and high-quality, digital two-channel profiles collected by the USGS in 1987. These data provide a superb source of information for hydrate mapping. The previous analysis of these data and other information, such as analog seismic data, magnetics and gravity surveys, sampling, and complete sidescan sonar coverage, provides us with a good understanding of the geology of the region (summarized in: Dillon et al., 1986; Dillon and Popenoe, 1988). In addition to the USGS data, one long-streamer research seismic line in the study area collected by the University of Texas and Woods Hole Oceanographic Institution is being analyzed at those institutions, heat flow data are being mapped at Woods Hole Oceanographic Institution, and chemical modeling is proceeding at the University of North Carolina, all with the support of this project.

Our goal to understand the volumes and distribution of gas hydrates will be met by using the digital seismic data. Effective use of these data requires a multi-step effort. The sequence of analyses that must be undertaken are organized as follows:

Seismic Processing

Two questions are addressed by computer-processing of seismic profiling data. (1.) What are the best estimates of velocities in the hydrate-cemented sediments for use in modeling? (2.) How can we standardize the seismic profile displays so that the displays can be correlated to modeled values of blanking, and, thus allow estimates of the amount of hydrate present?

Modeling

Basically the question to be addressed by seismic models is: What amount of hydrate is expected to produce a specific amount of blanking, given known characteristics of sediments in the study area and known attributes of hydrates?

Profile Interpreting

Once the profiles are processed and an interpretational model is accepted to provide a standard, the work consists of evaluating the profiles by comparing them to the standard, and interpreting the probable amounts of hydrate indicated by the seismic signatures.

Mapping

Finally, the profile interpretations are digitized and the estimations of hydrate are merged with navigation data. From this information we will make maps of hydrate distribution and derive estimates of hydrate volume.

RESULTS

Computer Processing of Seismic Reflection Data

Existing industry multichannel seismic data owned by the USGS and a small amount purchased for this project were reprocessed to emphasize the seismic signature created by gas hydrates. Locations of these profiles are shown by dashed tracks in Fig. 1. An example of reprocessed multichannel data is shown in Fig. 2. Note the strong reflection from the base of the gas-hydrate cemented zone (marked BSR) and the blanking (reduction in amplitude of the reflections) above the BSR. This blanking effect is particularly noticeable at the right side of the figure, where strong reflections from sedimentary strata (perhaps gas charged) below the BSR pass to the right through the BSR and thereafter show much reduced amplitude. The intensive analysis of industry profiles (dashed tracks, Fig. 1) was used to set parameters for the computer processing of the two-channel digital profiles (solid tracks, Fig. 1) in order to display the blanking effect most clearly. This standardized processing has been applied uniformly to all lines shown bold in Fig. 1 and processing is continuing .

Velocities in the most-blanked areas of the Blake Ridge-region profiles have been studied in great detail in this project using two approaches: (1.) analysis of a long-streamer, research profile using tau-P mapping at the University of Texas, Institute for Geophysics in Austin, TX, and (2.)

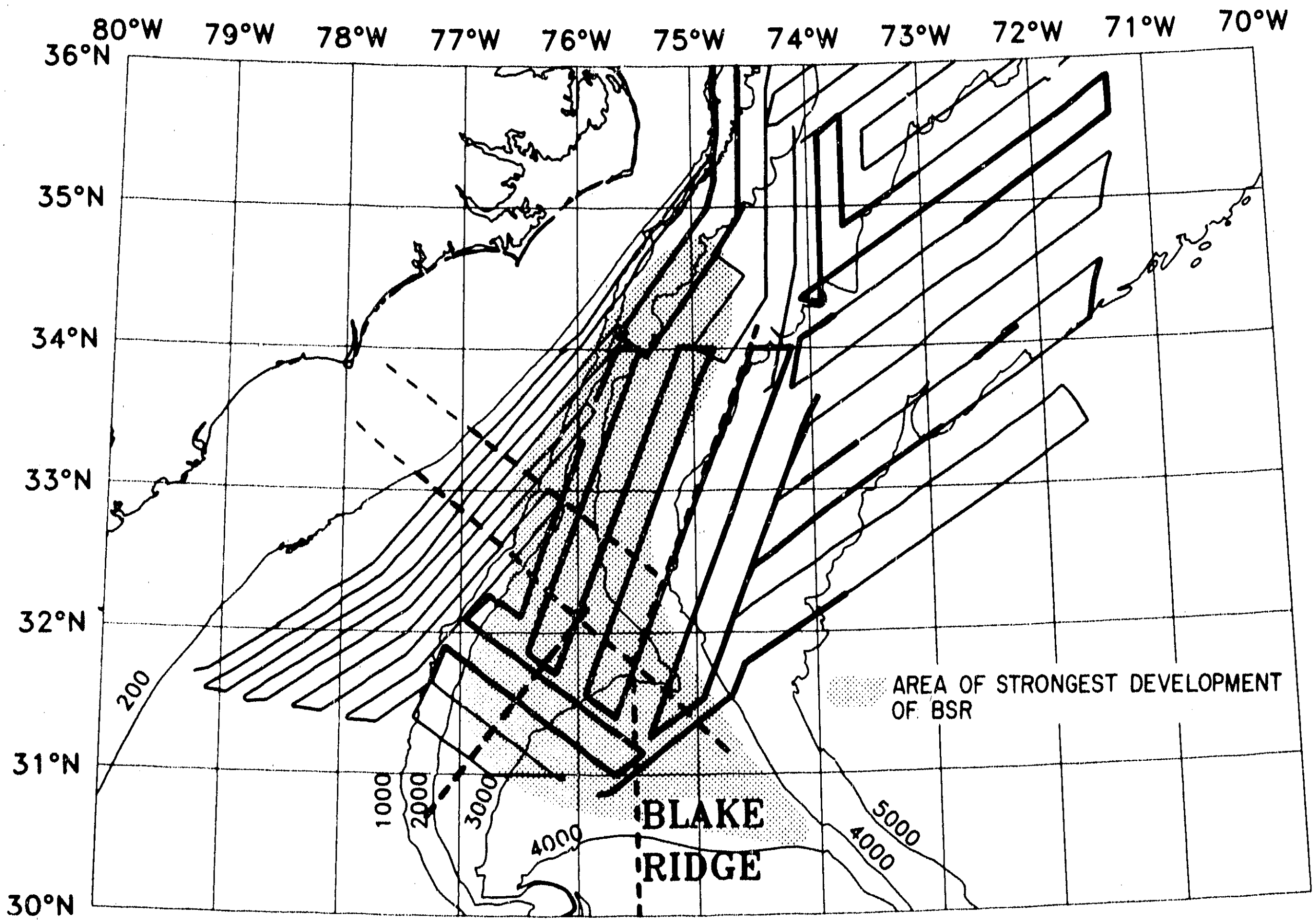

Figure 1. Locations of seismic profiles and indication of status of seismic data processing. Solid lines indicate two-channel, digital, high resolution profiles, dashed lines indicate commercial multichannel seismic profiles. Profiles with completed data processing are shown as bold lines.

analysis of the commercial multichannel profiles indicated in Fig. 1 at the USGS seismic processing center in Denver, CO, using an iterative, reflection coefficient technique. Despite the differences in methods, the two research groups have come to essentially identical conclusions, that maximum velocities in the most intensively blanked sediments are about 2.0-2.1 km/s. These velocities are somewhat below those estimated by some earlier workers and recently by Andreassen et al. (1990) using less sensitive techniques,. The new values are probably the best estimates of velocities to date, especially for the Blake Ridge area. Both the USGS and U. Texas work has shown that velocities beneath well-developed BSR's are about 1.6-1.7 km/s and that such velocities require the presence of free gas. The agreement between the velocity structures produced by the two groups is extremely encouraging and gives us much greater confidence in our mapping effort and in our understanding of the nature of hydrate cementation in these deposits.

Seismic Modeling for Interpretation of Gas-Hydrate Effects

In order to define the amount of gas hydrate in sediments by the blanking of reflections, we must model the effect of such blanking and relate it to specific amounts of hydrate cement. By using sediment porosity values from the Blake Ridge

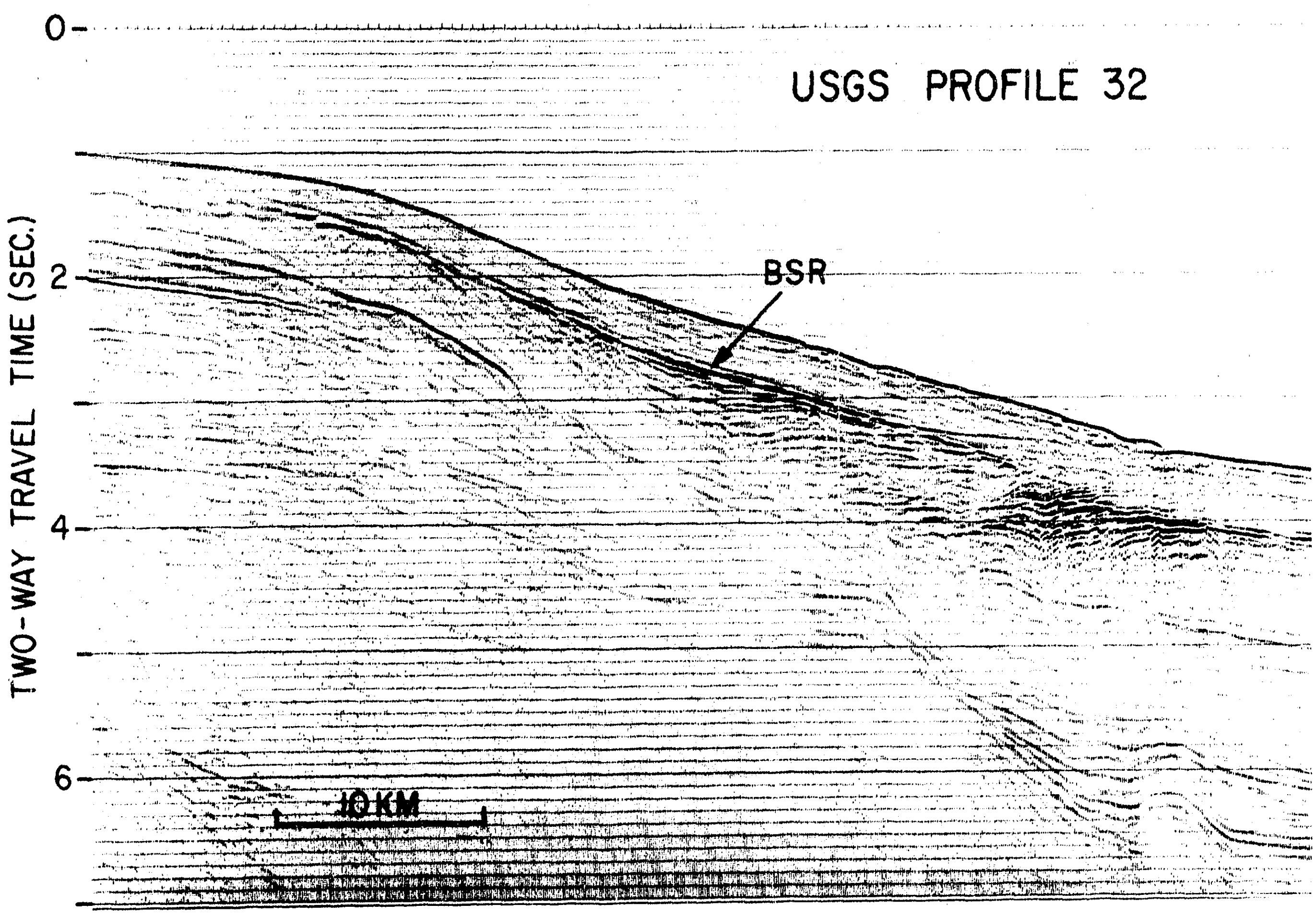

Figure 2. Example of reprocessed true-amplitude display of commercial multichannel seismic profile

obtained from Deep Sea Drilling Project cores, velocities from our new studies, and published hydrate velocities, we have calculated the amount of hydrate in the most intensively blanked sediments. In a sediment comparable to that of the Blake Ridge area (60% porosity), the maximum amount of hydrate that is allowed by the observed velocities would occur when 40% of the pore space were filled with gas hydrate. We assume that such a material is an end member, and, in our seismic modeling, we mix it with a similar deposit having no hydrate (the other end member), in order to model the range of possible blanking effects.

In a preliminary version of the model, the effect of various admixtures on reflection amplitudes is shown in Figs. 3 and 4 (Fig. 3 is calculated for a 12-68 Hz filter, comparable to our commercial multichannel data processing, whereas Fig. 4 is calculated for a 12-120 Hz filter, comparable to our two-channel, high-resolution processing parameters). The various model outputs are calculated for 0, 25, 50, 60, 70, 80, and 90% admixture of the end member hydrated sediment. The increase of blanking (reduction in amplitude of reflections) with increase of hydrate is apparent. Three classes of blanking have been assigned; the boundaries between classes representing a change in the power of reflections by a factor of two. The class boundaries are indicated on Figs. 3 and 4, and these classes may be related to overall average amounts of hydrate in bulk sediment, in our preliminary model, of approximately 6% (class 3), 15% (class 2), and 21% (class 1). Our intention is

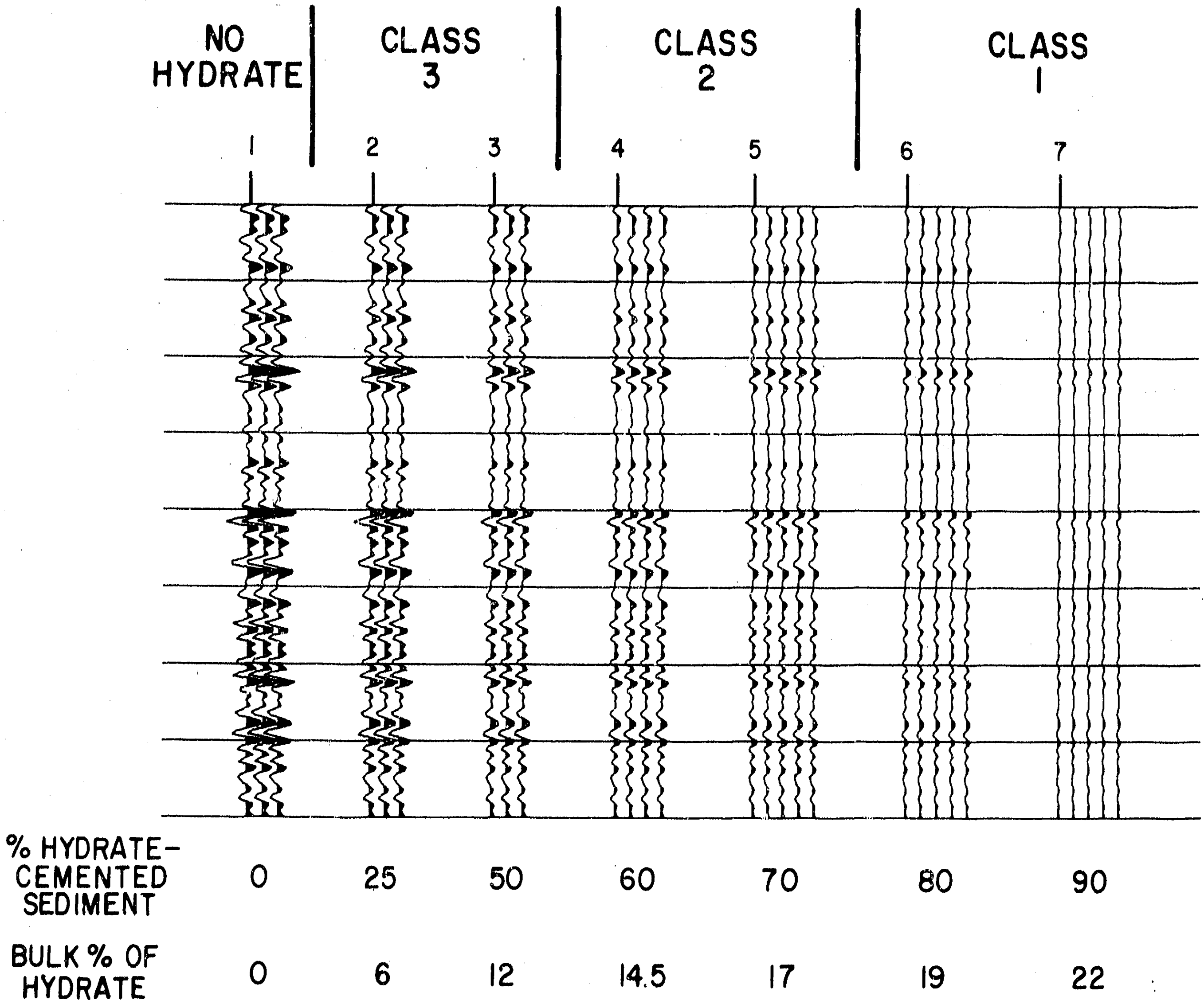

Figure 3. Models of blanking created by gas-hydrate cementation with various proportions of hydrate-cemented sediment. This model was created for a frequency filter of 12-68 Hz, comparable to commercial multichannel seismic data.

to map these classes across the region to estimate the amount of hydrate present. A model such as this has not been developed before and its application will be the first semi-quantitative approach to mapping hydrates.

Interpreting Profiles

Interpretation of profiles, which has just been initiated, consists of identifying locations where gas-hydrate cementation exists (generally by observing BSR's), then comparing the amount of blanking to the modeled effects (Figs. 3 and 4) and marking the areas covered by the various classes of blanking. An interpretation of classes in one of our reprocessed commercial multichannel profiles is shown in Fig. 5, and an example for one of the USGS 2-channel, high-resolution profiles is shown in Fig. 6.

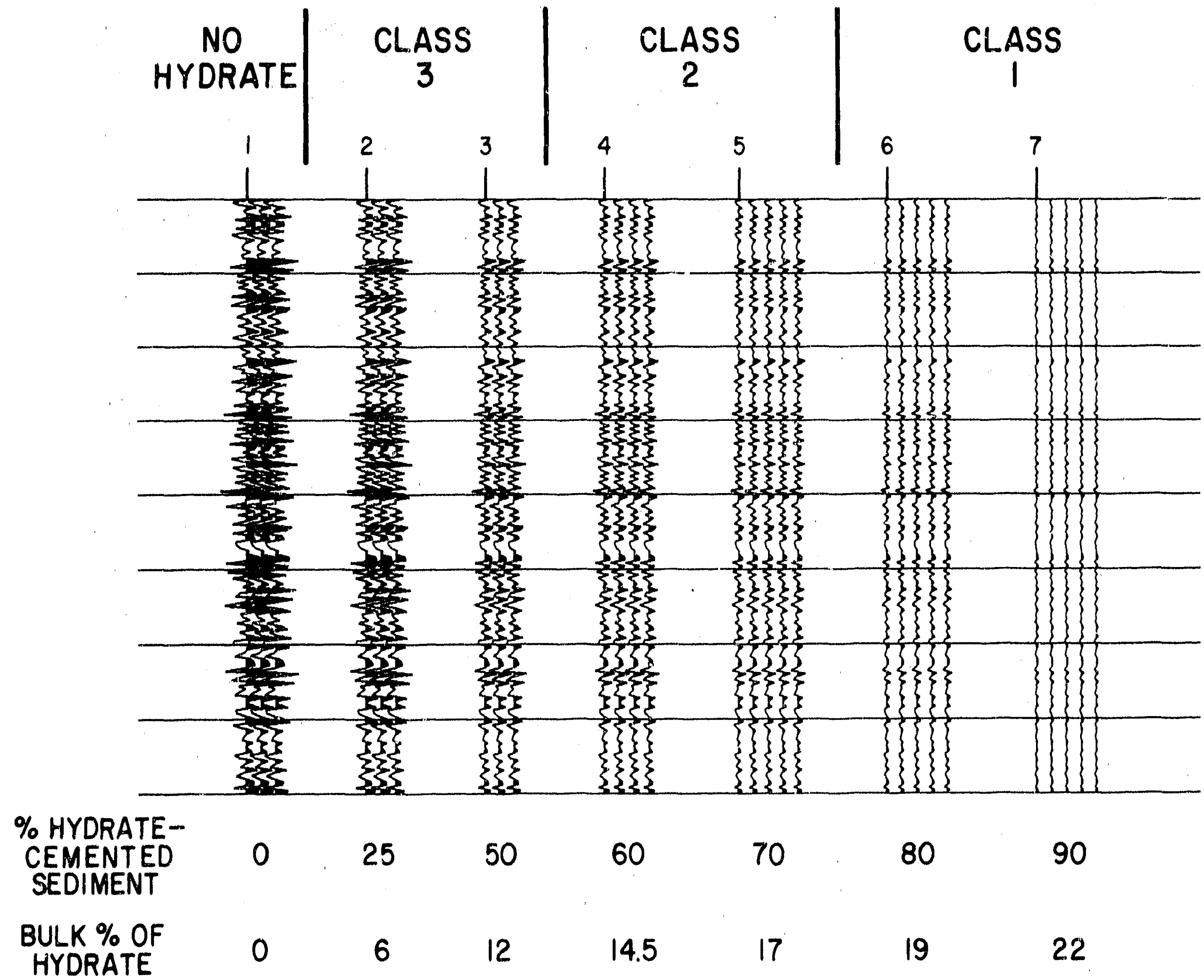

Figure 4. Models of blanking created by gas-hydrate cementation comparable to Figure 3, but calculated for a filter pass-band of 12-120 Hz, which is comparable to our high-resolution profiling data

Mapping

Mapping begins by digitizing the interpreted profile. An example of a digitized section is shown in Fig. 6. Then the thickness of pure hydrate is calculated from the digitized section at each location along a profile. Finally, this information is plotted on a map and volumes are integrated.

FUTURE WORK

Immediate plans call for the completion of seismic profile analysis in the Blake Ridge region and mapping of areas of different classes of blanking to create an estimate of the amounts of hydrate and gas in the region.

Future studies that can be accomplished without new field programs include the possibility of expansion of the mapping phase northward. Estimates of volumes of hydrates now seem feasible as a result of our seismic modeling work,

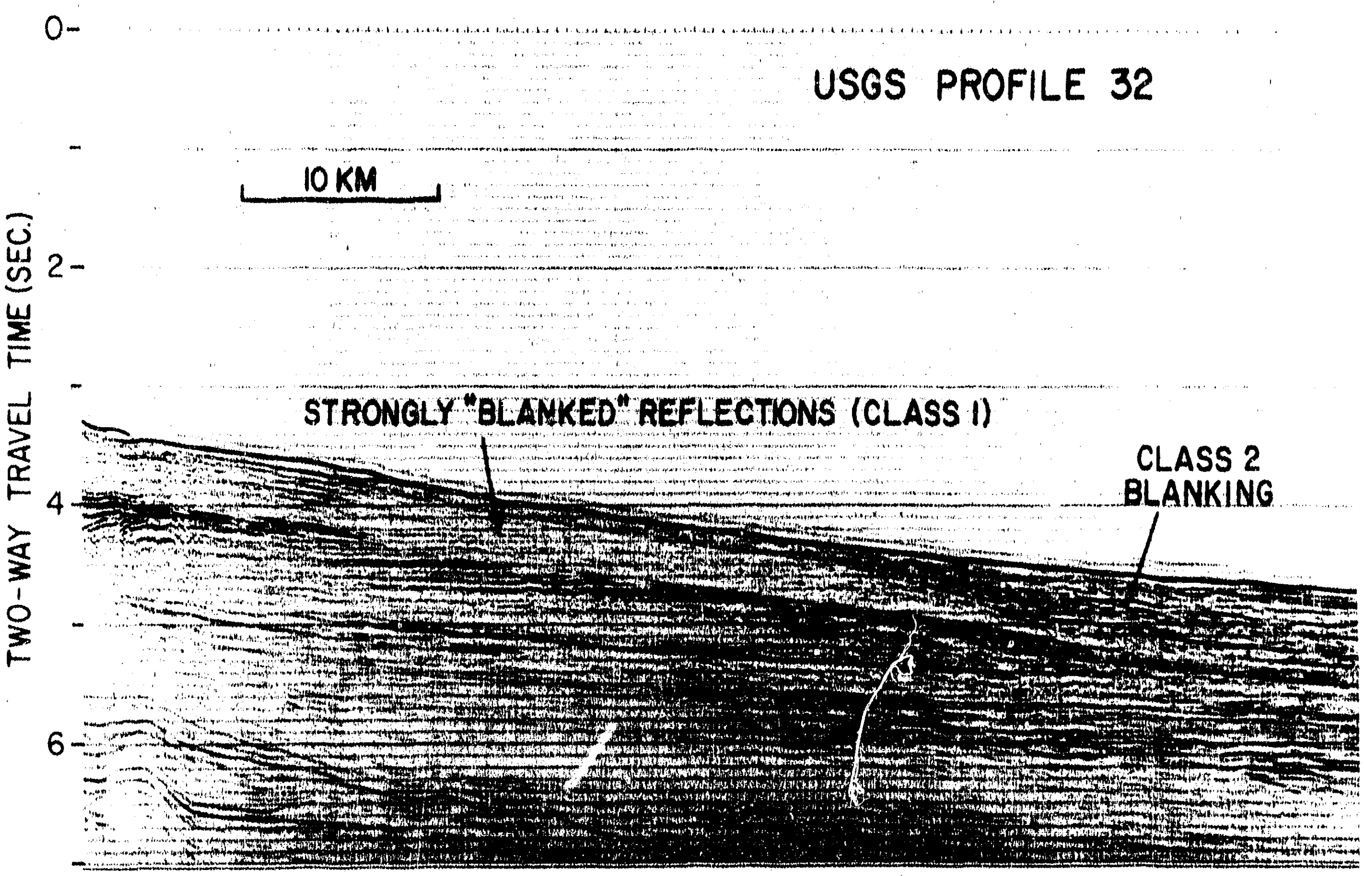

Figure 5. Examples of class 1 and class 2 blanking in a commercial multichannel seismic profile. Compare to the model standards shown in Figure 3.

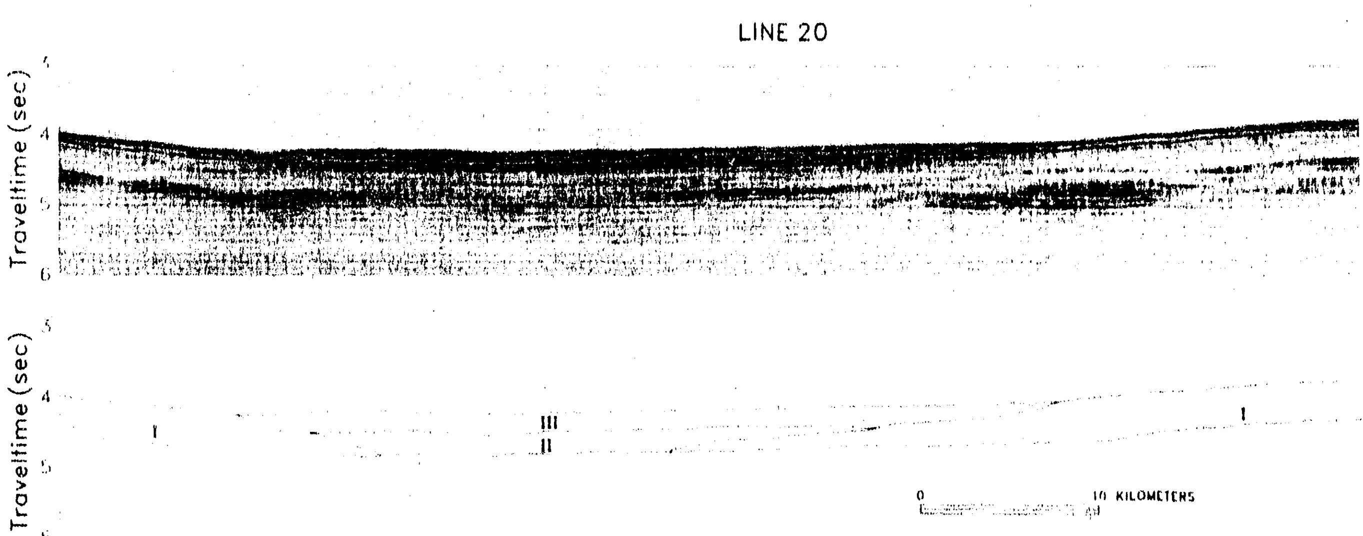

Figure 6. Example of two-channel, high resolution digital seismic profile showing the various classes of blanking. Compare to the model standards shown in Figure 4.

and such estimates could be made for the entire Atlantic Exclusive Economic Zone, with existing USGS data.

Preliminary analysis of loss of slope stability as a result of hydrate breakdown also can be made with available information, and this is likely to be a very important consideration. The continental slopes and rises are marked by numerous slides, and , off the U.S. east coast, heads of slides correlate with the shallow depth limit of gas-hydrate formation (Booth et al., 1988). Were those mass movements triggered by a phase change from gas hydrate to gas (plus water) as a result of hydrostatic pressure reduction caused by Pleistocene sea-level lowering (Dillon et al., in press; Paull, et al., submitted)? What would be the effect of reduction in pressure when attempting to produce gas from the hydrate? Theoretical analyses, followed by laboratory and field studies could provide answers.

Field seismic programs in the Blake Ridge region could collect data that would improve our evaluation of the amounts of hydrates and provide information on their variability. Analysis carried out at Woods Hole Oceanographic Institution as part of this project shows that using a near-bottom seismic source and sea floor receiver (an ocean bottom seismograph) would allow much more accurate analysis of sediment velocity. Although velocity estimates of gas-hydrate cemented sediments from surface source/receiver arrangements have been significantly improved during the first phase of this project, the analytical methods are basically limited because of the ray-path geometry. This limitation could be removed with data collected using near-sea floor instrumentation.

The variability of gas hydrate formation on a scale of kilometers is poorly known because our present grid spacing of seismic lines is about 25-30 km. A set of dense, precisely navigated small grids of digital high-resolution seismic reflection profiles covering areas around sites of the ocean-bottom velocity studies would allow us to analyze the spatial variability of gas hydrate distribution. Such analysis is critical to any possible commercial production of hydrate, and at present has not been done, to our knowledge.

Heat flow measurements correlated with seismic evidence for gas hydrates, plus coring, and ultimately drilling, would complete our understanding of hydrates in the Blake Ridge region.

To begin to study new areas, we would recommend the collection of long-streamer multichannel seismic data designed to maximize the capability for velocity calculations and create optimum imaging of gas hydrate effects.

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Session 4

Gas to Liquids

Natural Gas to Liquids

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ABSTRACT

The natural gas to liquids (NGTL) conversion research is a multidisciplinary effort focused on the development of an economic, one-step process that will convert natural gas to gasoline or distillates. This research effort is expected to produce process technology to convert natural gas to higher value uses and to provide a means of transporting natural gas from remote locations to the marketplace. One of the most promising options is to convert the gas to liquid fuels such as methanol or gasoline. Conventional technology using steam reforming is economically unfeasible. Other techniques, such as direct catalytic oxidative coupling, have potential for significant cost reduction. Therefore, this research effort has been initiated to develop new or improved techniques specifically related to rate and efficiency of conversion. In order to accomplish this research, two broad goals have been defined: (1) develop a method for converting natural gas to liquid fuels with acceptable conversion rates and selectivity to desired products, and (2) assess several catalytic and noncatalytic techniques through laboratory experiments, theoretical analyses, and systems analyses.

In pursuit of these goals, the approach to NGTL conversion research is as follows:

- Development of a major cost reduction through the exploration of new concepts to simplify the process, improve yields and selectivity, and improve separation and recovery of the product. The long-term research approach is to seek the ultimate, one-step conversion process with high yield, high selectivity, and high separation/recovery efficiency. The achievement of these goals will result in a competitive process on both large and small scales.

- Achievement of the major cost reduction through the development of catalytic, non-catalytic, and biologic processes, as well as trade-off evaluations of separation and recycle facilities for conversion and selectivity.

The NGTL conversion research project consists of the elements indicated above and a project management function. The project management function is a DOE function of planning, execution, control, and technical integration of the subprogram. Specific research activities are described here:

- New catalysts research includes assessment of several catalytic techniques through laboratory experiments, theoretical analysis, and systems analyses, in order to select the most promising methods for further development. The major part of the effort will be devoted to laboratory investigation of simplified, catalytic conversion methods for

production of ethylene and/or other intermediates that might be further converted to gasoline or other "end use" fuels.

- Noncatalytic processes research includes development of an understanding of the fundamental chemistry necessary to develop a process to partially oxidate methane to methanol by some form of exothermic reaction such as a plasma source, electromagnetic radiation, or other thermal initiation technique.

- Activities have been initiated to conduct and evaluate the use of biomimetic methods that use the desirable aspects of bio-conversion but avoid negative aspects such as slow reactions, large reactors, and product-separation problems.

- Preliminary plans to evaluate the development and enhancement of facilities for the separation, recycling, and collection of gas in disadvantaged areas of natural gas production. These facilities will be an integrated part of mobile conversion units.

- Future plans include preliminary activities to investigate the potential of converting natural gas into some form of high density fuel. The focus of the work is to enhance the development of cost-effective, high-density, and advanced fossil fuels for military and commercial applications. The categories of research will include the development of high-density diesel fuel, advanced industrial/aviation turbine fuels, and advanced high-energy, endothermic aviation fuel.

Accomplishments in FY 90 include the following activities and results:

- Testing provided preliminary information that could allow investigators to determine the influence of the reactor in conversion chemistry and aid in the evaluation of simulation and/or analytical models currently being developed.

- Studies were preformed that stabilize sodium pyrophosphate and allow the substitution of perovskite-type oxides for the normal cation. Although this substitution appears to be a superior catalyst, continued study will determine its value for natural gas conversion processes.

PETC's Natural Gas Conversion Program

CONTRACT INFORMATION

Contract Number	Not Applicable
Contractor	Not Applicable
Contractor Project Manager	Not Applicable
Principal Investigators	Not Applicable
PETC Project Manager	George Cinquegrane
Period of Performance	FY 1991

INTRODUCTION

The United States is confronted with a major shortage of domestic liquid hydrocarbon fuel supplies that threatens both the long-term energy security and the economic competitiveness of this country. The need for liquid fuels is forecast to be a persistent and critical element of the nation's energy requirements throughout this century and beyond. However, the supplies of petroleum hydrocarbons in the United States are finite and are being heavily drawn upon. Furthermore, low energy prices will tend to increase oil demand while intensifying the declining trends in both production capacity and additions to the recoverable reserve base. Domestic discovery rates of new reserves have been decreasing while the costs for exploration have been increasing. To enhance domestic supplies, techniques such as Enhanced Oil Recovery (EOR) can be applied to domestic oil fields to increase total recovery and prolong the availability of domestic supplies of petroleum. New areas can also be explored in the Arctic region and offshore for additional supplies. However, supply increases from such EOR activities and new frontier areas probably will be insufficient to reverse the slow but steady decline in oil production capacity.

Expanding the use of natural gas is one alternative for combating the increasing dependency on petroleum. The United States possesses a relatively abundant supply of conventional natural gas in the lower 48 states; however, vast amounts of unconventional natural gas exists in tight gas-bearing sandstone and limestone formations in the Southwest, the Rocky Mountains, and the northern Great Plains. Estimates of the latter resource range from 300 to 900 quads. Alaska also has over 33 quads of proven natural gas reserves. In addition, recoverable onshore and offshore undiscovered natural gas is estimated at over 100 quads.

Although evidence exists that the natural gas resource base is sufficient to meet anticipated growth in demand, the physical existence of supply does not necessarily equate to supply deliverability. Development of unconventional gas resources depends on improved extraction technology and on the feasibility of transporting the products to market. Where transporting natural gas via pipelines is not feasible, the conversion of the gas to liquid fuels or chemicals provides an alternative for the utilization of such reserves. Also, displacing petroleum with natural gas from the lower 48 states for the production of chemicals and/or chemical intermediates provides a means for extending our petroleum reserves and reducing our dependence on foreign suppliers.

DOE MISSION/PROGRAM OBJECTIVE

Fossil Energy's basic strategy is to identify research opportunities and conduct research in extracting, processing, and utilizing domestic fossil fuel resources. The overall goal of the Pittsburgh Energy Technology Center's (PETC) Natural Gas Conversion Program is to develop the scientific and engineering knowledge base with which industry can bring economically competitive and environmentally acceptable advanced technologies for the manufacture of hydrocarbon fuels and chemicals from natural gas when needed. The technical goal of the program is to seek significant innovative improvements over state-of-the-art technologies for the conversion of natural gas at domestic and remote sites to marketable fuels and chemicals.

The program is accomplished through staged development from laboratory scale to bench scale and finally to proof-of-concept scale. Maximum industrial involvement is sought in the program to facilitate commercial validity of the program and to achieve technology transfer.

CURRENT PROGRAM

The program focuses primarily on the direct conversion of natural gas to marketable liquid fuels and chemicals. Currently, the three most advanced direct conversion technologies being studied are the following:

- Oxyhydrochlorination
- Partial Oxidation
- Oxidative Coupling

The conversion of methane using enzymes is also being investigated but is still in its infancy.

Oxyhydrochlorination

A novel combination of two existing process concepts has been examined and appears capable of producing higher hydrocarbons from methane with high yield and selectivity. In the first-stage, chloromethanes are produced through oxyhydrochlorination of methane. In the second stage, chloromethane aromatization takes place to form gasoline (Figure 1). PETC was recently granted a patent on this two-step process.

Since the process continues to look economically promising ($32/BBL equivalent), a collaborative project between PETC and industry would accelerate development of this technology.

Partial Oxidation

A more efficient route for converting light hydrocarbons (e.g., methane) is via partial oxidation to form alcohols. For methane:

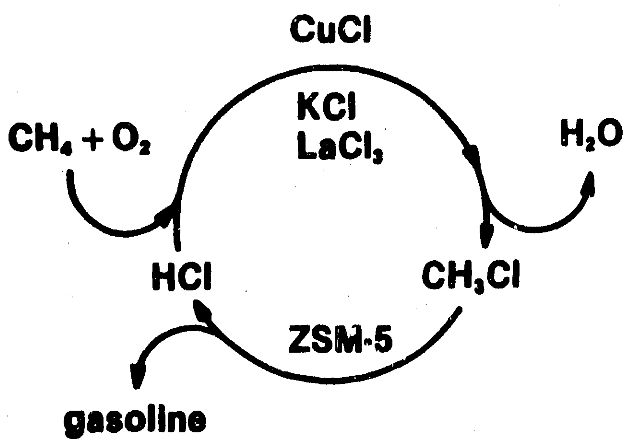


Figure 1. Cyclic Pathway for the Conversion of Methane to Gasoline by the Two-Stage Petc Process

$$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH \quad \Delta H = -30.7 \text{ kcal}$$

Such a process would substantially reduce the capital and energy requirements for methanol production. Researchers at the University of Manitoba have reported methanol selectivities of 80% at methane conversions of 8-10% using a Pyrex glass liner in the reactor. Amoco Oil is currently investigating various process modifications to enhance the yield of methanol.

The technology offers comparative simplicity, relatively low-heat transfer requirements, and economic attractiveness. The work at Amoco will continue throughout FY91.

Oxidative Coupling

Oxidative coupling of methane to produce ethylene has been the most widely investigated technology for the conversion of methane in recent years. Ethylene can then be further reacted to produce distillate products, which can be used directly as fuels or chemical feedstock. In FY90, the contract with Union Carbide Corporation for the oxidative coupling of methane was completed. No significant advances have been made and the economics remains unacceptable. Ironically, no group has yet achieved a selectivity/conversion comparable to an overall yield of >30%, the minimum yield estimated to be necessary for a commercially successful process.

No experimental work will be performed in FY91 on the oxidative coupling of methane.

Biomimetic Catalysts

One promising option exists that might, in the long term, lead to a viable alternative to the conventional process concepts. In FY90, Sandia National Laboratories continued a small effort in mimicking the biological process for converting methane to methanol. Structural features required for high activity and selectivity have been identified, and catalysts are being synthesized and characterized.

These special molecular catalysts are in their infancy but could develop into a promising approach, while possibly shedding light on catalytic improvements. Experimental work initially focused on the oxidation of ethane. The program will be extended to include methane.

FUTURE PROGRAM

Oxyhydrochlorination

The oxyhydrochlorination route is closer to the development stage than the routes involving direct conversion of methane to ethylene or methanol. The scaleup and commercialization of this route will require process engineering expertise that has the capability of resolving the many problems associated with handling large amounts of hydrogen chloride, methyl chloride, and other corrosive materials in this system.

- Dow Corning will further develop the first-stage and pilot it towards commercialization.
- Amoco will develop the second-stage with the goal of studying and optimizing chloromethane aromatization in the pilot plant.
- PETC will continue to focus on the enhancement of the methyl chloride selectivity with the base metal catalysts.

Partial Oxidation

Results from DOE engineering evaluations indicate that this technology would be the most economical and simplest for the direct conversion of natural gas to a liquid fuel provided the product selectivity to liquid product is 10% or higher. Amoco Oil Company will continue to investigate various process modifications to enhance the yield of methanol to a level that is deemed economical.

Oxidative Coupling

No significant advances have been made, and the economics remains unattractive. Commercialization of direct methane coupling is considered to be long range (10-15 years away).

Biomimetic Catalysts

Recent advances in biomimetic catalysts have resulted in developing molecular catalysts. Some high potential catalytic methods are in the conceptual stage at Sandia and need further exploration.

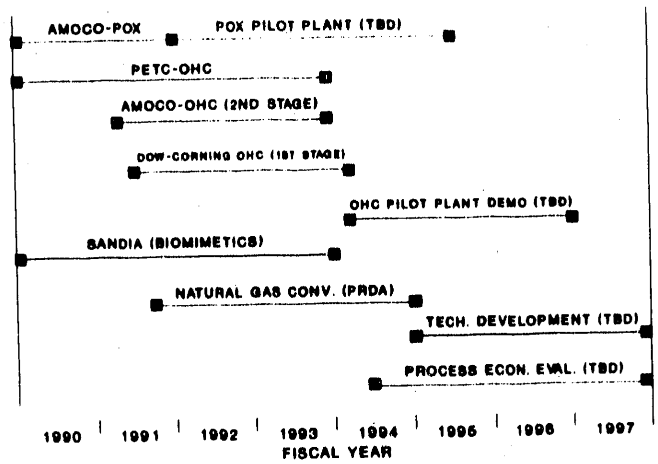
Other Implementation Approaches

A workshop on the direct conversion of natural gas to liquid fuels and chemicals was held on November 6, 1990. At this meeting, the state-of-the-art and future research needs of all applicable technologies were addressed, including partial oxidation, oxidative coupling, oxyhydrochlorination, and biomimetics. An industrial perspective of the need for such technologies was also presented. From this workshop, several areas were identified that have potential for significant developments. This information will be used in developing a Program Research and Development Announcement (PRDA). Three to five research contracts are anticipated to be awarded in FY91 as a result of this solicitation.

Figure 2 summarizes the program schedule for the development of PETC's Natural Gas Processing Research program. Activities identified under technical development and process economic evaluation will follow the successful completion of the PRDA. The integrated efforts are expected to develop a comprehensive understanding of not only the basic science of conversion chemistry but also technical and economic solutions to the natural gas conversion issue.

Figure 2

NATURAL GAS CONVERSION
PROGRAM SCHEDULE



Gas Phase and Catalytic Partial Oxidation Reactions of Methane and Oxygen

CONTRACT INFORMATION

Contract Number	FEW-6030
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Contractor Project Manager	Michael W. Droege, L-325 (415) 422-0155/FTS 532-0155
Principal Investigators	M.W. Droege L.M. Hair
Metc Project Manager	Rodney D. Malone
Period Of Performance	FY 1990

Schedule/Milestones

Milestones for FY90 were to complete a numerical chemical kinetic modeling of the gas-phase reactions of methane with oxygen and possible effects on catalyst reactions.

OBJECTIVE

The effective utilization of "remote" natural gas requires research aimed at developing catalyzed reactions using oxygen that lead to partial oxidation or oxidative coupling of methane. Despite intensive efforts by many researchers, the best yields to C2 hydrocarbons have been in the 20 to 30 % range, generally accomplished with catalysts which include an alkali metal on an alkali earth oxide, e.g., Li/MgO. Our efforts have been focused on the development of a general chemical kinetic model to predict C2 yield and describe product trends as a function of generalized catalyst behavior.

BACKGROUND

The study of reactions that facilitate a partial oxidation or oxidative coupling reaction of methane using oxygen is an area of current active research motivated by the desire to discover technologies that directly convert methane to liquid fuels and higher value chemicals. The future for methane conversion and natural gas processing depends on the development of catalyzed routes that directly convert methane to liquid hydrocarbons. The thermodynamically allowed, general reaction that transforms methane (CH_4) to higher hydrocarbons, summarized below,

$$nCH_4 + (y/2)O_2 \text{ ----> } C_nH_{4n-2y} + yH_2O$$

is an oxidative process that requires the use of a catalyst to facilitate the reaction. Non-catalyzed, simple thermal reactions of methane and oxygen require very high operating temperatures (700-800 °C) and, as a result, the desired product yield of hydrocarbons is unacceptably low, in large part due to the uncontrolled over-oxidation of methane to carbon monoxide (CO) and carbon dioxide (CO_2). The key to upgrading methane to liquid fuels is the controlled catalytic activation of the C–H bond preventing over-oxidation.

PROJECT DESCRIPTION

The major emphasis of this project is the development of new catalyst materials which facilitate reactions that convert methane to liquid fuels. Reactions of interest include partial oxidation (forming methanol and formaldehyde) or oxidative coupling (forming ethane and ethylene) of methane using oxygen. Our research efforts have focused both on the development of new catalysts that select and accelerate the partial oxidation or coupling reactions and on describing the gas phase reactions of methane and oxygen that lead to methane oxidation and their relationship to catalyzed reactions. In this report, we describe our recent work in developing a chemical kinetic model designed to predict C2 yield and describe product trends as a function of generalized catalyst behavior.

RESULTS AND DISCUSSION

During the study of some of our new catalysts, we observed, for even chemically quite distinct materials, similar reactivity patterns. An examination of the literature[1] shows that despite the wide range of catalyst materials that have been studied under an equally wide variety of experimental conditions, a common reactivity pattern emerges. This pattern, characterized by the inverse relationship between methane conversion and product selectivity, has been observed for both partial oxidation and oxidative coupling reactions.[1b] In considering the experimental conditions needed to study these catalysts in simulated process situations, it became clear that a significant potential exists for the appearance of non-catalyzed, thermally-activated gas-phase reactions of methane and oxygen. Under the appropriate experimental conditions these reactions can be quite important. Experimentally, in a quartz reactor at 800 °C with a 3:1 methane-to-oxygen ratio and residence times of 5-10 sec, we have observed significant conversion of methane (30%) to light hydrocarbons and CO_x with appreciable selectivity (25%) to C_2^+ components due solely to these background reactions. In order to better understand and describe the contribution of these background reactions during catalyzed reactions, we have employed a chemical kinetic model (HCT) developed at this Laboratory to describe these homogeneous gas phase reactions. This model has been developed over a number of years primarily for the study of methane and natural gas combustion.

Previously, we used this model to describe homogenous reactions that lead to the partial oxidation of methane.[2-4] It was tested against a series of experimental reactions comparing the effects of various reaction parameters. We found that use of the model allowed us to quickly and accurately predict the magnitude of the background reactions.

Recently, we have applied this computational model for the description of generalized catalytic reactions of methane with oxygen. Beginning with the thermal gas-phase model, we have included global reactions for the catalytic formation of partial oxidation products and their decomposition. The model now predicts catalyst performance as a function of product yield. This allows us to quickly assess the viability of new candidate catalysts for the conversion of methane to liquid hydrocarbons. Additionally, the model also suggests that for these types of catalysts obeying this mechanism (oxide materials operating at high temperatures), there appears to be a limit on the expected yield of C_2 products at about 30%.

Description of Chemical Kinetic Model

The chemical kinetic model used in the present study is the HCT (Hydrodynamics, Chemical kinetics, and Transport) model.[5] This model solves the coupled equations of conservation of mass, momentum, and energy, and determines each chemical species concentration in finite difference form. For this study, the reactor is assumed to be essentially a plug flow system where spatial variations in velocity, temperature, and species concentrations in the radial direction and diffusion of energy and species in the axial direction are assumed to be negligible. As a result, spatial changes in species concentration and temperature can be replaced by time variations. Thus only the energy equation and the species conservation equations must be solved. Surface reactions at the reactor wall were not considered. In the numerical model, coupling between the different chemical species takes place through the chemical kinetic terms, and these terms are introduced into the model through a detailed chemical reaction mechanism.[6]

The plug flow model is an approximation of the experimental reactor and assumes a radially-uniform velocity and temperature profile. In the actual reactor under isothermal conditions, the flow will attain a fully developed (parabolic) velocity and temperature profile after a short entry length of about 1 mm, since the Reynolds number (based on the inner diameter of the reactor) is about 3. The plug flow approximation was invoked since it results in considerable simplification of the numerical model.

The chemical reaction mechanism used here has developed from a number of studies of methane and natural gas combustion.[7-9] This mechanism has been extensively validated in a series of studies where numerical results were compared to experimental results from static reactors, stirred reactors, shock tubes, flames, and flow reactors.[10-17] The reaction mechanism does not consider carbon containing species C_3 or greater.

Inclusion of Catalytic Reactions

Methane Activation. A schematic of the mechanistic pathways leading to the gas-phase oxidation of methane by oxygen is shown in Figure 1. We have added reactions to the chemical kinetic mechanism to treat the effect of introducing an oxidative coupling catalyst. It is generally assumed that the effectiveness of oxidative coupling catalysts stems from their ability to activate methane. Thus, the first step was to determine the effect of methane activation alone. There is considerable experimental evidence to suggest that these catalysts react primarily by abstracting a hydrogen atom from methane. Sensitivity analysis of the gas-phase reaction mechanism suggests that the rate of this step (rate of methyl radical production) has a significant impact on the predicted C_2 yield. We can model the effect of methyl radical production by a catalyst as the global step shown in equation 1. This reaction assumes that the sole function of the catalyst is to produce methyl radical from methane and that

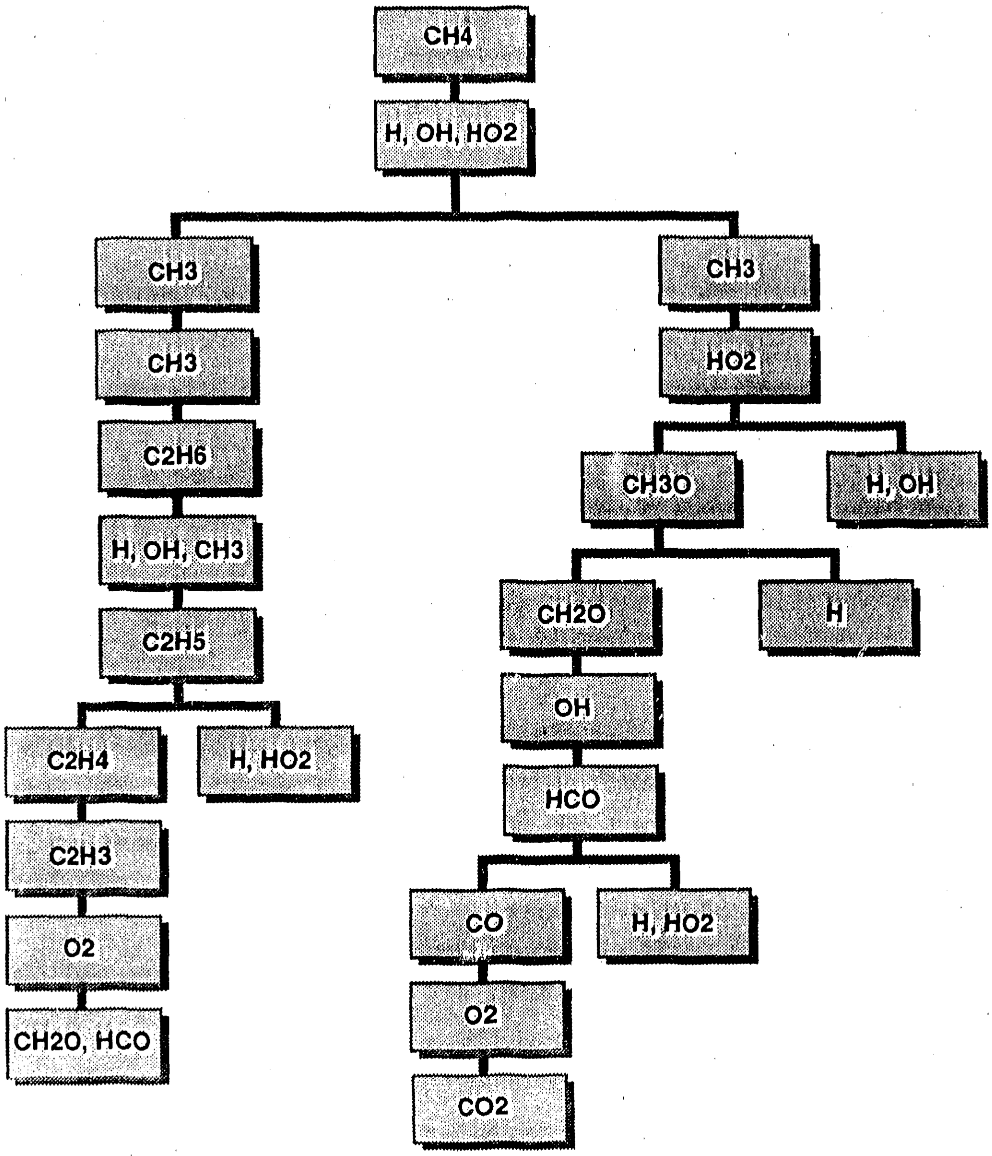

Figure 1. Schematic of Gas-Phase Mechanism for Methane Oxidation

subsequent reactions of these radicals occur by gas-phase processes.

$$CH_4 + 1/4\ O_2 \text{ ----> } CH_3 + 1/2\ H_2O \qquad (1)$$

We assumed the reaction rate is given by the expression of equation 2. The dependence of the rate on $[O_2]^a$ serves to turn off the catalytic reaction when the gas phase oxygen is depleted.

$$\text{rate} = k_1[CH_4][O_2]^a \qquad (2)$$

In this equation, k_1 is rate constant for catalytic methane activation (catalytic methyl radical production). The exponent "a" is set to

1.0 since we do not know the series of elementary reactions. Computationally, it appears that the overall reaction is not critically dependent on the value of the "a" exponent.

A series of calculations were performed with the above "catalytic" reaction added to the gas-phase chemical kinetic mechanism in order to explore the effect of catalyst activity (k_1) on predicted C_2 yield. The initial conditions considered were a 2:1 ratio of CH_4:O_2 in a 75% Ar mixture at 750 °C and 1 atm. Figure 2 shows the result of these calculations. It is predicted that as , k_1, increases from 10^{-2} to 10^7 1/Ms, the C_2 yield increases from about 0.4 to 70%. When no catalyst is present, the gas-phase reactions result in a C_2 yield of about 0.4% under these conditions of high dilution. The calculations indicate that the catalyst does not substantially affect the yield until the catalytic methane activation rate constant reaches about 10^1 1/Ms. At this point, approximately half of the rate of feed methane conversion occurs by gas-phase reactions alone. One role of the catalyst appears to be as an initiator for the gas-phase reaction.

Values of k_1 and the corresponding C_2 yield observed experimentally for several methane coupling catalysts are compared in Fig. 3. In calculating k_1 from experimental data, it was assumed that the rate of methyl radical production was equal to the rate of methane conversion and was, therefore, determined from the experimental methane feed rate and the final methane conversion. The rate constant, k_1, was then found by dividing that rate by the methane and oxygen concentrations in the feed at reaction temperature. As shown in Figure 3, the model does an excellent job of predicting the

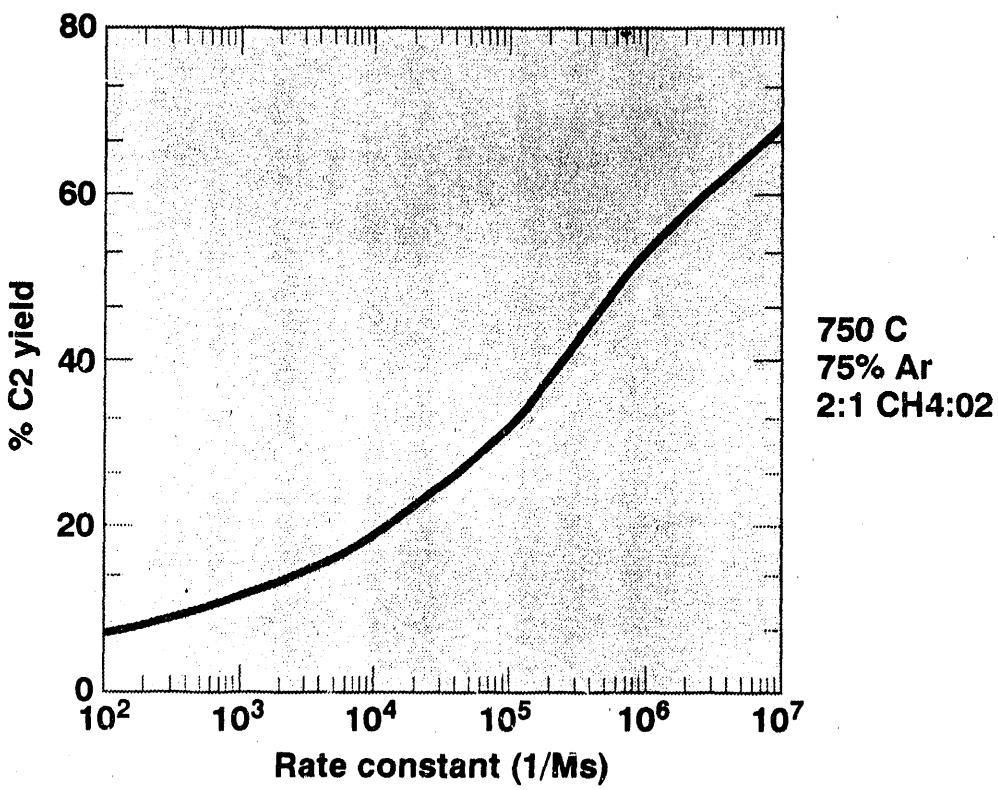

Figure 2. Plot of Predicted C_2 Yield vs Rate Constant (10 sec residence time)

trend of the experimental data. It also suggests that for very active catalysts producing methyl radicals, high yields of C_2 products would be expected.

Overall, this simple modification of the gas-phase kinetic model to include a global catalytic step that only produces methyl radical agrees reasonably well with experimental data. However, experimental C_2 yields greater that about 30% are not observed and it is clear that the catalytic/gas-phase model does not account for the apparent yield barrier.

carbon oxides. We have expanded the mechanism of HCT to account for such product decomposition reactions as shown schematically in Figure 4. The reaction steps included in the product decomposition mechanism were obtained from reported experimental studies of C_2 reactions over methane coupling catalysts.[18-20] We have used this expanded mechanism to investigate the effect of catalytic decomposition of products on C_2 yield and to predict ultimate C_2 yields.

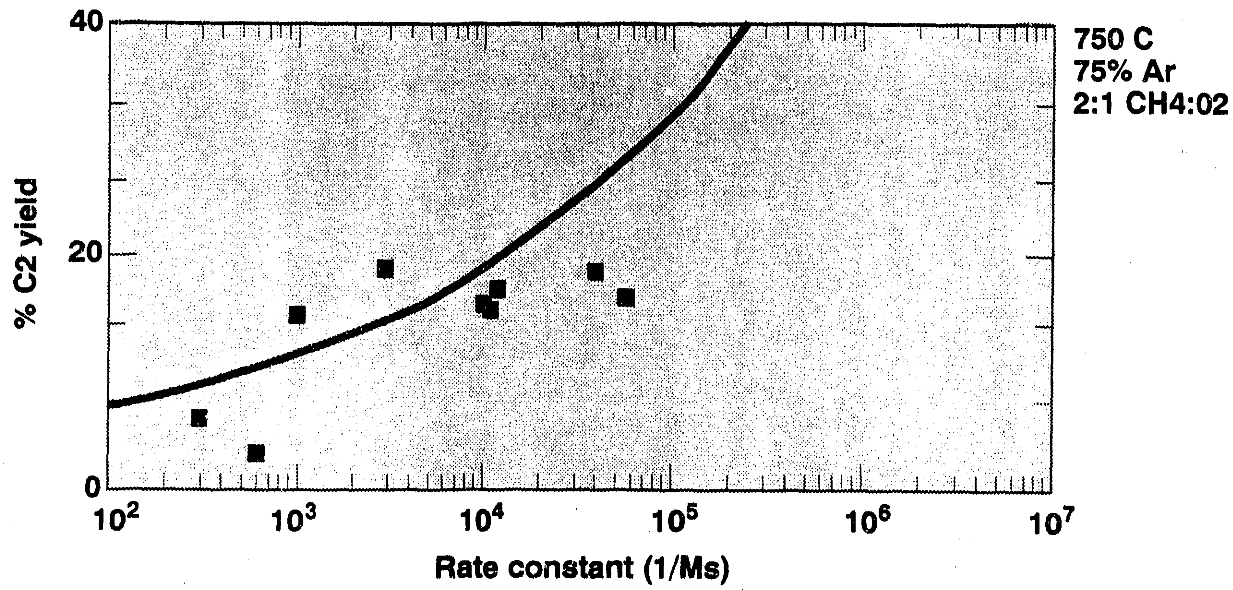

Figure 3. Comparison of Predicted C_2 Yield vs Rate Curve With Experimental Values

Catalytic Product Hydrocarbon Decomposition. It can be assumed that catalysts that activate methane and result in coupling products (C_2's) are also likely to activate and further react with such products. These catalysts may react with product hydrocarbons by hydrogen atom abstraction producing free radicals for subsequent gas-phase decomposition processes or by direct catalytic decomposition reactions that oxidize the hydrocarbon products to

Figure 5 shows the results of these calculations and compares them to the original k_1 vs yield curve obtained for the case with catalytic methane activation but no catalytic decomposition of products (figure 3). Since the literature is not consistent in the evaluation of the rates for C_2 decomposition over oxidative coupling catalysts, two different cases are presented in Figure 5. In general, the two cases track each other closely with a gradual increase of predicted C_2 yield

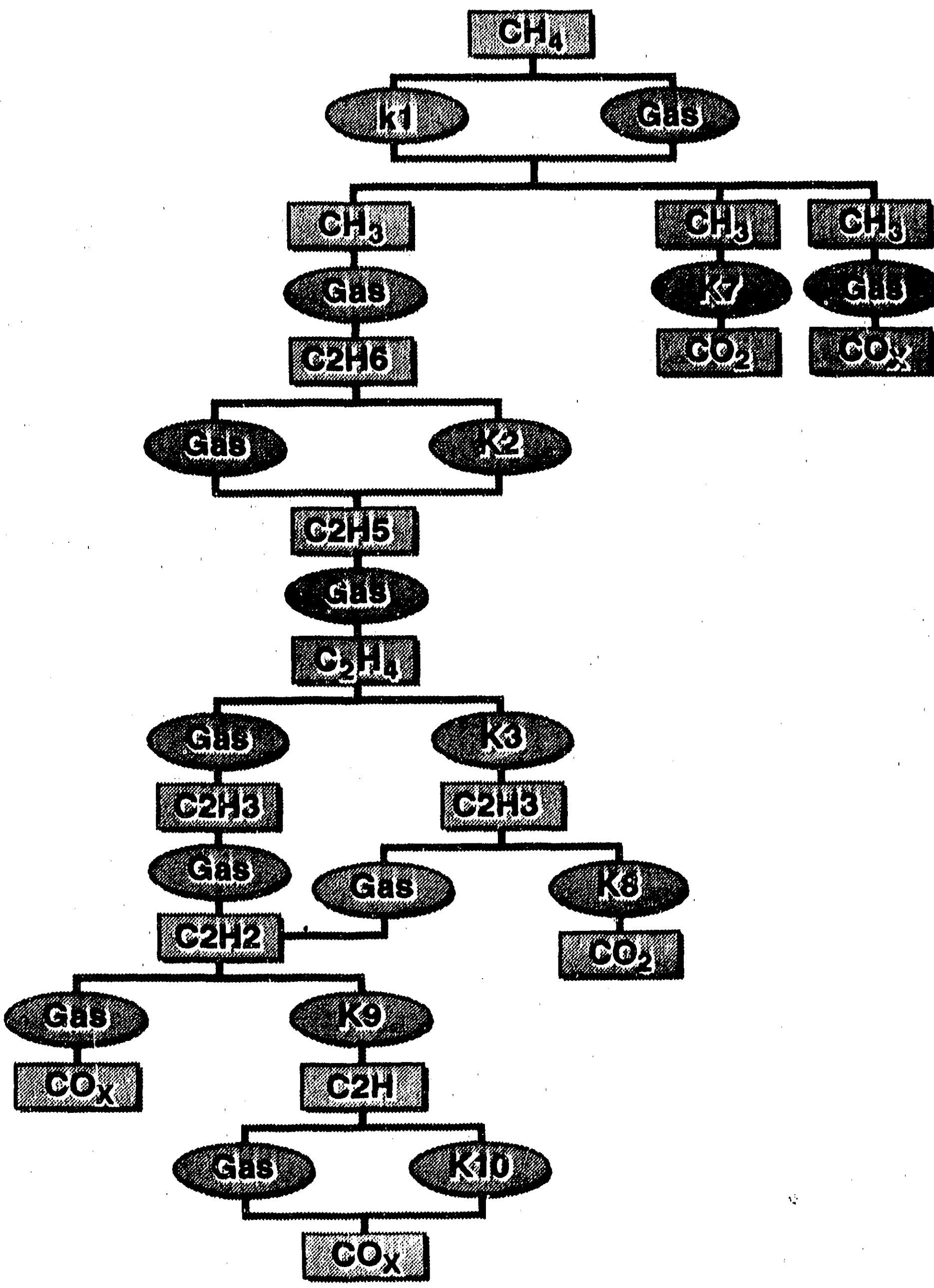

Figure 4. Schematic of Gas-Phase Methane Oxidation Mechanism Including Catalyzed Methane Activation and Product Decomposition Steps ("gas" indicates gas-phase processes; "k" indicate catalyzed processes)

with increasing k_1 up to 10^4-10^5 1/Ms. At this point, there is a rapid decrease in C_2 yield as k_1 increases. The calculations indicate that an upper limit in catalytic activity (k_1) exists for maximum C_2 yield. Catalysts that are too active for methyl radical production facilitate product decomposition. It appears, therefore, that the reactions for catalytic methyl radical production and product decomposition are coupled and that a balance point between activation and decomposition exists for optimum C_2 yield. These calculations suggest that a k_1 of about 10^5 will lead to maximum C_2 yields. Using this value and returning to the original k_1 vs yield curve obtained for the case with catalytic methane activation but no catalytic decomposition of products (Figure 3), it can be predicted that the maximum yield for oxidative coupling catalysts obeying this mechanism is about 30%. This value is consistent with yield barrier widely reported in the methane coupling literature.

result, future work will focus on the evaluation of new mechanistic pathways for the selective partial oxidation of methane.

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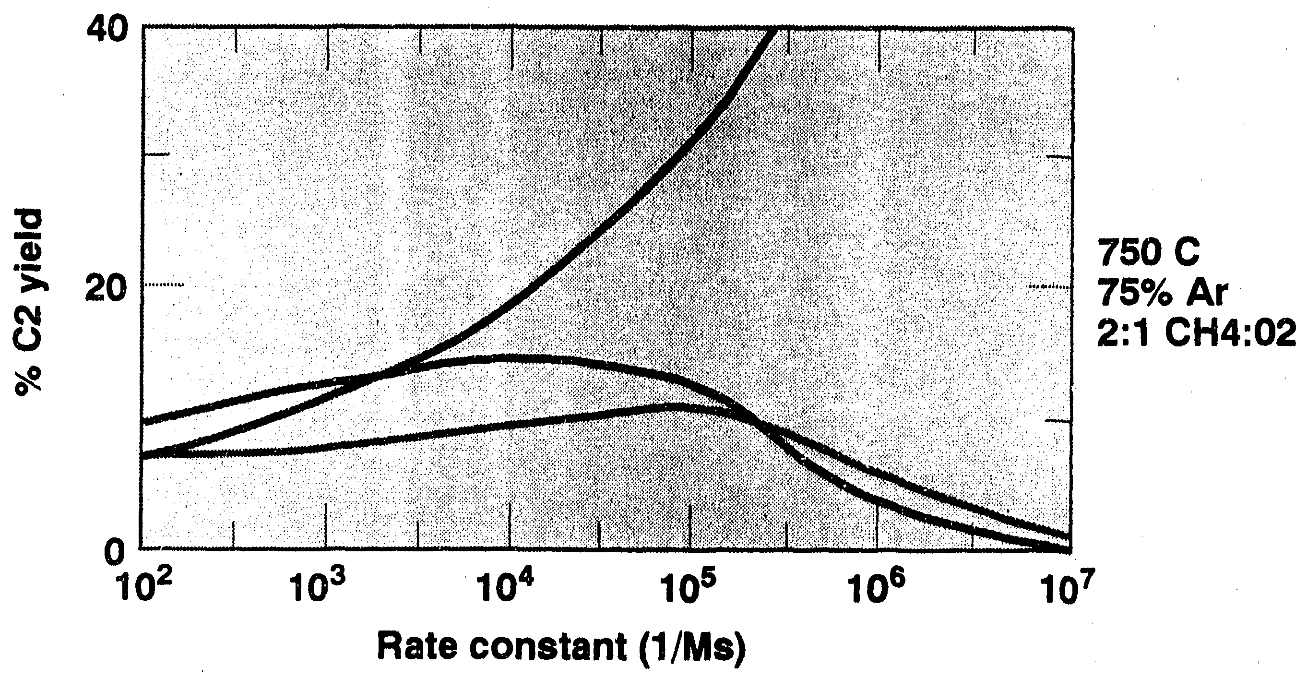

Figure 5. Plot of the Effect of C_2 Decomposition Steps on Predicted C_2 Yield (rising black line is the same curve as shown in Fig. 2 - no C_2 decomposition; falling black and grey lines are two different calculations including C_2 decomposition)

FUTURE WORK

The results above suggest that methane oxidative coupling catalysts operating at high temperatures (oxide catalysts) will likely be limited in their potential for use as process catalysts for natural gas conversion. As a

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Methane Oxidation Over Dual Redox Catalysts

CONTRACT INFORMATION

Contract Number	DE-FG21-89MC26039
Contractor	Lehigh University Zettlemoyer Center for Surface Studies and Department of Chemistry Bethelehem, PA 18015 (215) 758-3577 or 758-3486
Contractor Project Manager	Kamil Klier Richard G. Herman
Principal Investigators	Kamil Klier Richard G. Herman
METC Project Manager	Rodney D. Malone
Period of Performance	January 1, 1989 to December 31, 1991

OBJECTIVES

The objectives of this research are to achieve and understand the partial oxidation of methane to oxygenates, especially methanol, and C_2 hydrocarbons over dual redox catalysts. The catalysts are based on oxidic materials that will exhibit structural and thermal stability for long reactor lifetimes. A continuous flow reactor system with oxygen or air as the oxidizing gas, rather than nitrous oxide, is being utilized over a wide range of pressures (1-100 atmospheres) and temperatures (≤1000°C) in order to maximize the space time yields of the desired products. All of the investigated processes are catalytic and are aimed at minimizing gas phase reactions.

BACKGROUND INFORMATION

Saturated linear hydrocarbons, particularly methane, are major components of natural gas and of the gas from certain gasifiers. While methane makes an excellent gaseous fuel, it is desirable to convert it to higher molecular weight products for transportation, storage and for utilization as chemical feedstock. The desired reactions are shown below, for the sake of simplifying the discussion, for methane only:

$$CH_4 + 0.5\ O_2 \rightarrow CH_3OH \qquad [1]$$

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \qquad [2]$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad [3]$$

$$2CH_4 + 0.5\ O_2 \rightarrow C_2H_6 + H_2O \qquad [4]$$

While the oxidative coupling paths [3] and [4] show considerable promise, it is evident from the patent examples that the process conditions are still quite severe, in particular that the reaction temperature, in the range 650-800°C, is still too high. Reactions leading to oxygenates (Equations [1] and [2]) are more difficult to conduct selectively, but they have been identified as being very desirable, particularly the oxidation to methanol (F. Dautzenberg, Preprints, Symposium on Methane Activation, Conversion, and Utilization, PACIFICHEM '89, International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Paper No. 170 (1989)). At the same time, the standard free energy of all the oxidations [1]-[4] is negative over a wide range of temperatures, establishing a thermodynamic driving force for these reactions even at room temperature should an effective catalyst be found. More practical considerations led us to seek a desirable temperature range of 350-650°C. The lower limit of 350°C is based on experience with the dehydration of most oxide catalysts, which lose water at temperatures ≤ 350°C. The upper limit of 650°C is in the range of temperatures at which uncontrolled free radical reactions will occur and often will lower the selectivity by driving the oxidation process to CO and CO_2. Hence it is desirable to investigate and develop catalysts that promote partial oxidations of methane to C_2^+ hydrocarbons, methanol, or formaldehyde in the temperature range 350-650°C.

The investigators submit that suitable conditions for the desired type of oxidation catalysis (Reactions [1] and [2]) exist on the surfaces of oxides that are doubly promoted by transition metal ion redox couples so that one redox couple is utilized for activation of oxygen and another for the conversion of methyl fragments to carbocations or carboanions. It is proposed that the active oxygen is utilized for hydrogen abstraction from the methane molecule and the methyl carbocation pathway yields methanol while the methyl carboanion pathway yields ethylene or ethane. Reaction conditions are also important and it is well established empirically that methanol by reaction [1] is favored over formaldehyde by reaction [2] at high pressures. However, the effect of pressure on oxidative coupling reactions [3] and [4] has so far not been systematically explored and therefore pressure is an important reaction variable in the proposed studies.

PROJECT DESCRIPTION

Dual redox and redox-Lewis acid systems doped into oxide and silicate matrices are being investigated for selective oxidation of methane to methanol, formaldehyde, and C_2 hydrocarbons. As an oxide matrix, zinc oxide was initially chosen because of its well-understood defect chemistry. As a silicate matrix, the initial choice was ZSM-5 zeolite framework-substituted with iron. All of these matrices were to be cationically exchanged with copper or iron or both. In fact, all systems proposed for the present investigations contain copper because of its suitable redox potential Cu^{I}/Cu^{II} and its dopability into binary oxides. The catalyst systems that prove promising for the selective oxidation of methane will be subjected to high pressure tests aiming at further enhancement of both activity and selectivity.

The proposed research is divided into three tasks. **Task 1** deals with preparation and testing of catalyst systems such as Cu^{I}/Fe^{III} and $Cu_2{}^{I}/Sn^{IV}$ doped into ZnO. **Task 2** aims at the extension of the Anderson-Tsai methanol chemistry in CuFeZSM-5 with oxygen used as oxidizing gas, and at potential modifications of the double redox systems to produce C_2 hydrocarbons including extending the framework composition and pore size to that accessible in other silicates such as the stannosilicates. **Task 3** involves optimization studies and high pressure studies of methane conversion over the most promising selective oxidation catalysts investigated in the previous tasks.

RESULTS

The catalysts so far studied are ZnO and ZSM-5 zeolites that are doubly doped with a redox couple such as Cu^{I}/Cu^{II} and another dopant that executes either a redox or a Lewis acid function. initially the Fe^{II}/Fe^{III}, Sn^{II}/Sn^{IV}, and Pd^{o}/Pd^{II} couples. These dopants are planted by a valence pinning doping process in the zinc oxide matrix and by framework substitution/ion exchange in ZSM-5 zeolite.

Dual Redox ZnO-Based Catalysts. The doping of these catalysts was carried out by physically mixing the solid oxides together and calcining at 1000°C for 22 hr in air.

Testing was carried out with 0.114 g of the ZnO-based catalysts positioned in a 6 mm OD quartz reaction that narrowed into a 2 mm ID capillary immediately below the catalyst bed to allow rapid product removal. At ambient pressure, a CH_4/air = 1/1 reactant was employed at a gas hourly space velocity of 70,000 ℓ/kg catal/hr. Initial product analyses were achieved by sequential on-line injection into parallel columns consisting of a 3.2 mm x 2 m Porapak Q packed fused silica column and a 3.2 mm x 2 m packed 13X zeolite column in a Hewlett-Packard 5730A chromatograph interfaced with a 5880A integrator. Testing at each temperature was typically carried out for 2.5-3.5 hr while carrying out the gas chromatographic analyses every six min. Condensable water-soluble products were collected in two water-filled scrubbers in series, the first was kept at room temperature and the second at 0°C. Formaldehyde was qualitatively detected by the West and Sen chromotropic acid method (R. W. West and B. Sen, Z. Anal. Chem., **153**, 177 (1956)) and was quantitatively determined by the modified Romijn's iodmetric titration (G. Romijn, Z. Anal. Chem., **36**, 19 (1877)).

Appreciable conversion of reactants was noted over the Cu/Fe/ZnO = 1/1/98 and Cu/Sn/ZnO = 1.0/0.5/98.5 catalysts at 450°C, and more than 90% of the oxygen was consumed over these catalysts at higher temperatures of 750-800°C. Two main temperature regions could be distinguished with respect to the performance of the catalysts. One region occurs below 700°C with formaldehyde as a principal partial oxidation product (along with CO_2), and a second region is observed above 750°C, where mainly C_2 coupling products together with CO. Relative to the undoped ZnO, those catalysts doped with Cu and Fe or Sn exhibited **significant improvement in the CH_2O selectivity**, especially in the low temperature range. For example, at 600°C the Cu/Fe/ZnO, Cu/Sn/ZnO, and ZnO catalysts showed 25.3, 13.7, and 2.5 carbon atom% CH_2O selectivities, respectively, while the remainder of the product was CO_2. The simultaneous decrease of associated CO_2 selectivity in the low temperature range of 450-650°C indicates that the dopants depress the ZnO activity for deep oxidation to form CO_2 and promote the formation of formaldehyde.

As the temperature was increased to 650°C and above, the CH_2O selectivities decreased, but the space time yields significantly increased over these catalysts because of the higher methane conversion rates. In the high temperature range, i.e.

>700°C, the activity of the ZnO catalyst uniformly increased and the decrease in the selectivity toward CH_2O was due to the significant increase in the yield and selectivity of the C_2 products. The Cu/Fe/ZnO and Cu/Sn/ZnO catalysts exhibited maximum space time yields at 750°C of 76 and 38 g CH_2O/kg catal/hr, respectively.

Although the Cu/Sn/ZnO catalyst exhibited behavior that was similar to the Cu/Fe/ZnO catalyst, it was appreciably less selective toward formaldehyde. Therefore, it was not investigated further.

As pointed out, without the metal dopants the low surface area ZnO produced principally CO_2 and C_2 coupling products as the oxidation products. It was shown that doping the ZnO with transition metal ions caused a *selectivity switch* to occur in the methane oxidation reaction from CO_2 toward CH_2O at lower temperatures and from C_2 products toward CH_2O at higher temperatures. Large amounts of CO_2 were formed over both promoted and unpromoted catalysts, and the overall selectivity toward formaldehyde decreased with increasing temperature.

To probe the role of each of the dopants in the Cu/Fe/ZnO catalyst, the $Fe_{0.01}Zn_{0.99}O$ and $Cu_{0.01}Zn_{0.99}O$ singly doped catalysts were synthetized and successfully tested under continuous flow steady-state conditions given above for methane conversion. It was observed that addition of the redox Fe cation dopant to the ZnO matrix significantly promoted the catalytic conversion of methane to *formaldehyde* at the designated reaction conditions, via a large increase of the CH_2O selectivity, giving the maximum space time yield of 78 g/kg catal/h at 800°C. However, a pronounced decrease of the overall activity of the Fe/ZnO catalyst, in comparison to the pure zinc oxide, was also observed. In contrast to the doubly doped Cu/Fe/ZnO catalyst, the single Fe dopant caused no apparent *shift in the selectivity* from C_2 coupling products toward formaldehyde, since there was a high selectivity for C_2 products at high temperature that was approximately the same as for the ZnO catalyst. A feature of the single Fe dopant was a sharp depression of the activity toward the deep oxidation reaction that yields CO_2, which corresponded to the enhancement in CH_2O selectivity.

The single copper dopant, in comparison to the iron dopant, showed lower CH_2O, CO, and C_2 selectivities and much higher CO_2 selectivity. However, the total activity of the Cu/ZnO catalyst was *greater* than that of the Fe/ZnO catalyst. Above 650°C, the Cu/ZnO catalyst, relative to ZnO, exhibited a shift in selectivity from C_2 products to CO_2. However, the Cu/ZnO material also catalyzed a severe deposition of coke at temperatures of 750-800°C.

Characterization of the ZnO-Based Catalysts. The ZnO-based catalysts have been fully characterized in terms of morphology, surface area, bulk and surface compositions, and chemical states of the dopants. In particular, surface analyses of the ZnO-based catalysts were carried out using a SCIENTA ESCA-300 X-Ray Photoelectron Spectrometer (XPS) equipped with a rotating anode X-ray source (Al K_α, $h\nu$ = 1486.6 eV), double focusing X-ray monochromator, hemispherical photoelectron analyser, and computer controlled instrument operation and data aquisition system. A Submonolayer Science flood gun was used for charge neutralization of the samples. The survey scans were recorded in the binding energy range of 0-1050 eV with a pass energy 300 eV. For quantitative analysis, 20-40 eV scans were taken with a pass energy of 75 eV. The typical background pressure was better than 10^{-9} Torr. The spectral smoothing, deconvolution, and integration was performed using a software package provided by SCIENTA. The peak positions were calibrated relative to the Zn $2p_{3/2}$ (BE = 1021.7 eV) and adventitious carbon 1s line (BE = 285 eV). In order to reduce the differential charging of the samples, revealed by preliminary experiments to be significant, and possible contamination of the catalysts by contact with the ambient atmosphere, the following procedure for sample preparation was employed. After firing at 1000°C, the catalysts were sealed at that temperature in quartz ampoules and transferred to a glove-bag filled with dry oxygen-free nitrogen. The catalyst powder was pressed into indium foil, which was then attached by means of a drop of gallium to a glass plate. The entire assemble was then held to the stainless steel sample holder with beryllium brass clips. The samples were introduced into the spectrometer chamber without any contact with ambient atmosphere since the transfer was carried out through the N_2-filled glove-bag.

Analyses of the surface concentrations of dopants by XPS demonstrated in all cases that the surface of the catalysts was dopant enriched, as shown in Table 1. The extent of surface enrichment does not depend very strongly on the particular dopant. However, in the case of Fe/ZnO the surface enrichment was distinctly lower than those of Cu/ZnO or Fe/Cu/ZnO. The doubly doped Cu/Fe/ZnO sample showed nearly equal enrichment (3.5%) at the surface by both dopants, preserving the bulk Cu/Fe stoichiometry ratio, which is consistent with the formation of the charge balancing Cu^{+}-Fe^{3+} couples in the divalent ZnO matrix.

TABLE 1

Determination of the Surface Concentrations as Ratios of the Cu and Fe Dopants in Zinc Oxide Catalysts.

Catalyst	Cu/ZnO	Fe/ZnO	Cu/Fe/ZnO
Bulk Cu/Zn	0.0101	--	0.0102
Bulk Fe/Zn	--	0.0101	0.0112
Surface Cu/Zn	0.035	--	0.036
Surface Fe/Zn	--	0.028	0.035

The BE of the copper $2p_{3/2}$ level of 932.8-933.2 eV in all catalysts under study, together with the lack of any evidence of satelite structure on the high binding energy side indicated that this line could be assigned to Cu^{+} in tetrahedral coordination. The position of the $2p_{3/2}$ peak of iron at 710.9 eV for Fe/ZnO and at 711.2 eV for Cu/Fe/ZnO, along with the presence of a broad satelite at about 720 eV, agrees with the assignment of iron as Fe^{3+}, presumably also in a tetrahedral position.

By HR-ESCA, it was shown that the dopants were in Cu(I) and Fe(III) valence states in tetrahedral coordination and both to be enriched on the catalyst surface to 3.5% surface concentration. Thus, the Cu(I) and Fe(III) substituents for Zn(II) make an ion pair that is subject to Coulombic attraction and travels in equimolar stoichiometric quantities from the bulk to the catalyst surface. This indicates that the Cu/Fe/ZnO preparation method is a successful technique for synthesizing these catalysts.

Cu/Fe Doped ZSM-5 Zeolite. The purpose of the present work is to verify, enhance, and modify the activity and selectivity of the CuFe ZSM-5 and sodalite catalysts. The oxidizing gas will be O_2 in the catalyst testing program to be carried out. The two catalysts have been synthesized *via* a three stage procedure as outlined below.

Stage One involves the synthesis of the HFeZSM-5 or HFe sodalite materials. In both cases, the syntheses are carried out so that the Fe^{3+} ions are located in the zeolite structures in place of the usual Al^{3+} in the analogous aluminosilicate framework structures. The following synthesis procedures are based on literature methods (R. Szostak and T. L. Thomas, J. Chem. Soc., Chem. Commun., 113 (1986) and R. Szostak, V. Nair, and T. L. Thomas, J. Chem. Soc., Faraday Trans. 1, **83**, 487 (1987)) and are described in detail in our quarterly technical reports.

One of the major features of the synthesis procedure is the use of low molecular weight silica species as the silica source (N-brand silica, $Na_2SiO_3 \cdot 5H_2O$; PQ Corp.) for the formation of the ferricilicate gels. By doing so, precipitation of rust-red iron hydroxide at the high pH of ≈10 necessary for the zeolite crystallization and complex formation of the iron with the organic template agent, which makes the FeO_2^- species unavailable for incorporation into the zeolite framework, could be avoided. At pH values of 3-4, Fe^{3+} has the ability to precipitate low molecular weight silica species through complex formation. Once the iron is complexed in this way, the pH can be increased to basic conditions without the above undesirable effects occurring.

The synthesis procedure utilized to reach the required high pH conditions initially began with a highly acidic aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich Chem., ACS reagent grade) that was acidified with 96% H_2SO_4. To this solution was added an aqueous solution of the N-brand silica, and the formation of a pale yellow gel was observed. To prepare HFeZSM-5 zeolite, a template solution of tetrapropylammonium bromide (Aldrich Chem., reagent grade) was then added. To prepare HFe sodalite, a solution of tetramethylammonium chloride (Aldrich Chem., reagent grade) was added. The pH was finally adjusted to between 9 and 11 by adding 50% NaOH.

The resultant gels were heated in a Teflon-lined autoclave (Parr Instrument 125 ml high pressure bomb) at 170°C for three days under autogenic pressure. The autoclaves were mounted in a heated laboratory oven and continuously rotated on a specially constructed device at 90 rpm (see Figure 9 for the axis of rotation). In this manner, white solids were obtained that were filtered, washed, and dried at 100°C. X-Ray powder diffraction was used to confirm the synthesis of highly crystalline ferrisilicate zeolites with the ZSM-5 and sodalite structures.

After removal of the template by decomposition at 550°C, a yellow or tan coloring of the previously white samples seems to indicate some removal of the iron from the framework. This was observed under both N_2 and air environments. This process of template decomposition is still under investigation, as are techniques to remove the apparent extra-framework Fe^{3+} species created by the decomposition procedure.

However, a method to remove the extra-framework iron that has been used consists of stirring the zeolite in a solution prepared by mixing a 10% NaCl solution with distilled water (with a vol ratio of 1:7) at 70°C. While stirring, $Na_2S_2O_4$ (0.25 g/g zeolite) was added, and the mixture was equilibrated for 15 min. The suspension was centrifuged and washed with distilled water to remove the residual chloride ions from the solid. This extraction/washing procedure was repeated five times, and then the zeolite sample was filtered and washed with distilled water.

The described process primarily involves a reduction of Fe^{3+} ions to Fe^{2+} by the $S_2O_4^{2-}$ anion and thereafter ion exchange of the Fe^{2+} by Na^+. However, this process might not be completely adequate. Upon adding the $S_2O_4^{2-}$ solution, a green coloring of the sample occurred, indicating a reduction of the Fe^{2+} ions. However, only in the first two extractions did the washing solution become green, which showed that the extra-framework Fe^{2+} salts were removed from the zeolite. Following this, the final filtering and washing on a Buchner filter led to a reoxidation of Fe^{2+} species as concluded from the color change from the green of the wet zeolite to yellow for the filter dried sample.

The crystallinity, ZSM-5 structural framework, and purity of the ion exchanged (Cu^{2+},NH_4^+)FeZSM-5 was verified by X-ray powder diffraction (XRD) at different points in the synthesis procedure, and comparisons were made with the XRD pattern obtained with a Mobil-synthesized ZSM-5 sample.

In <u>Stage Two</u> of the synthesis procedure, the acidic forms of the zeolites are obtained by ion exchange of the zeolites with 0.1 N NH_4Cl solution followed by a thermal treatment at 400°C under O_2 to remove NH_3 and retain H^+.

<u>Stage Three</u> produces the Cu^{2+} exchanged forms of the Fe^{3+} substituted zeolites. This is accomplished by equilibration of the zeolites with excess 0.1 M $CuSO_4$ solution, followed by washing and drying under mild conditons.

The CuFeZSM-5 catalyst was tested using 0.1 g portions loaded into a 9 mm OD quartz reactor that narrowed into a 2 mm ID capillary immediately below the catalyst bed to allow rapid product removal. A quartz wool plug of 4-5 mm in height below the bed was used to position the catalyst in the reactor. Initially, the zeolite catalyst with particle size in the 45-75 μm range was loaded alone in the reactor. However, the pressure drop in the reactor became too high with this packed bed, and therefore the zeolite catalyst was diluted with quartz particles having dimensions in the 200-400 μm range.

Catalytic testing was carried out at ambient pressure with a reactant mixture of CH_4/air = 1:1 with GHSV = 70,000 ℓ/kg catal/h in the temperature range of 400-850°C, which are the same reaction conditions as used with the Cu/Fe/ZnO catalyst. The same analytical methods were used to quantitatively determine the products formed as a function of reaction temperature.

At 400°C, the conversion of reactants was detected, and the products consisted of CH_2O, CO_2, CO, and H_2O. A sharp increase in the oxygen conversion was noted at 600°C, and at 850°C complete O_2 consumption was achieved. The associated temperature dependence of methane conversion exhibited a parallel behavior and achieved a maximum conversion level of ≈17% at 850°C.

Two main temperature regions can be distinguished with respect to the performance of the catalyst. One region occurred below 650-700°C with CH_2O as a partial oxidation product. A second region could be observed above

700°C, where mainly C_2 coupling products, together with large amounts of CO, were formed. It was observed that the selectivity toward CH_2O was very low over the whole temperature range. The remainder of the products at the lower temperatures were CO_2 and CO. Whether the CO was formed as a direct oxidation product of CH_4 or as a decomposition product of CH_2O has not yet been established. However, the presence of H_2 as a product at higher temperatures could favor the second pathway. In this case, the decomposition of CH_2O could be induced by slow diffusion out of the zeolite channels of the formed primary products. It was noted that the selectivity to CO remained constant (≈5-6%) until oxidative coupling to C_2 products was initiated. Thus, the behavior of CO and C_2 products selectivities tend to parallel one another. Even though the CH_2O selectivity was very low, e.g. ≈ 2% at 750 and 800°C, a high space time yield of 113 g CH_2O/kg catal/hr was obtained at 800°C.

The effect of the quartz beads that are used to dilute the catalysts being tested for the selective oxidation of methane to oxygenates were investigated and compared with the activities and selectivities observed over the CuFeZSM-5 zeolite catalyst. It was found that the ability of the quartz beads to activate methane below 700°C was very low. However, above 700°C, appreciable conversion of methane and oxygen was observed, and the principal oxidation product consisted of the C_2 hydrocarbons. At the same time, there was a significantly increasing selectivity towards CO relative to CO_2 and CH_2O.

The catalytic data obtained over quartz beads allow the activities and selectivities observed over the diluted CuFeZSM-5 zeolite catalyst to be corrected for the activity of the quartz beads. It is concluded that catalytic testing for selective CH_4 oxidation can be performed in a reliable manner below 700°C, but at higher temperatures the presence of the quartz beads diluent must be considered in determining the activity and selectivity of the catalyst. The principal effect of the quartz beads on the selectivity at high temperature is to enhance the C_2 selectivity at the expense of CO_2.

<u>Supported Pd Catalysts for Methane Activation</u>. A 0.58 wt% Pd/SiO_2 catalyst was prepared and tested for oxidation of methane, and it was observed that the methane was converted to CO_2 over a large temperature range. Of special interest to this study was the demonstration that the Pd catalyst exhibited high activity in the low temperature range of 325-340°C for the complete oxidation of CH_4. In order to combine the low temperature activity of the Pd catalysts with the partial oxidation selectivity of the Cu/Fe/ZnO catalysts, a series of Pd-doped Cu/Fe/ZnO catalysts have been prepared and are currently being tested.

<u>Conclusions</u>. This research project has been on schedule during the first two years. Accomplishments include the following:

i. Doubly promoted ZnO-based and ZSM-5 zeolite-based catalysts have been successfully prepared, whereby it has been shown that with the ZnO-based catalyst the Cu(I) and Fe(III) substituents for Zn(II) make an ion pair that is subject to Coulombic attraction and travel in equimolar stoichiometric quantities from the bulk to the catalyst surface.

ii. Significant yields of formaldehyde have been obtained over the Cu/Fe/ZnO catalyst under steady state conditions.

iii. It has been demonstrated that formaldehyde formation from a CH_4/air = 1 mixture is induced by a *selectivity switch* from C_2 hydrocarbon products over ZnO to the oxygenated product over doubly Cu/Fe-doped ZnO to yield up to 76 g CH_2O/kg catal/hr.

iv. The Cu/Fe/ZnO catalyst has been fully characterized by X-ray powder diffraction, surface area determinations, and high resolution X-ray photoelectron spectroscopy (HR-ESCA).

v. The CuFeZSM-5 catalyst produced a relatively high space time yield of formaldehyde, but the selectivity was very low.

vi. Supported Pd catalysts by are very active catalysts for the complete oxidation of methane at low reaction temperatures.

Details of this research are described in quarterly technical progress reports DOE/MC/26039-1 through DOE/MC/26039-7.

FUTURE WORK

Evidence suggests that C_2 hydrocarbon yields are favored at high temperatures and low pressures and that formaldehyde is favored at low temperatures and higher pressures. Methanol is expected to be the product at still higher pressures due to the probable intermediacy of surface methoxides in the reaction cycle leading to oxygenates. Experiments are designed to examine this hypothesis, and variation of reaction conditions aims at optimization of the process for either methanol or C_2 hydrocarbons.

The research carried out in Years 1 and 2 of this research program was centered on the preparation, characterization, and catalytic testing of the zinc oxide-based and ZSM-5 zeolite catalysts for the selective oxidation of methane. A newly constructed high temperature catalyst testing system is being used for the methane oxidation studies. It has been found that specially prepared Cu/Fe/ZnO and Cu/Fe/ZSM-5 zeolite catalysts produce, at ambient pressure, formaldehyde from methane in high space time yields with O_2 as the oxidant.

Since it was found that supported Pd catalysts are very active in the oxidation of CH_4 at mild temperatures, e.g. 350±100°C, the selective Cu/Fe/ZnO catalysts are being surface doped with small amounts of Pd in an attempt to increase the activity of these catalysts at temperature lower than 650°C. Following these experiments, the research that will be carried out during Year 3 of this project will be centered on the testing of the most promising catalysts under *high pressure* conditions that are expected to favor and enhance the selective oxidation of methane to methanol.

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Methane to Methanol Conversion

CONTRACT INFORMATION

Contract Number	FEW A180
Contractor	Los Alamos National Laboratory P. O. Box 1663, MS G738 Los Alamos, NM 87545
Contractor Project Manager	Francis T. Finch
Principal Investigators	Wayne C. Danen John L. Lyman Richard C. Oldenborg Cheryl K. Rofer Monty J. Ferris
METC Project Manager	Rodney D. Malone
Contract Period of Performance	May 1, 1984 to September 30, 1990

Schedule and Milestones

FY91 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
Reactor Experiments	—	—	—	—	—	—							
Analysis							—	—	—				
FY92 Plan										—	—	—	
Report													—

OBJECTIVES

The objective of this research effort is to understand the fundamental chemistry necessary to develop a process to effect the partial oxidation of methane to methanol using air or oxygen. The goal is to develop an economically viable process to convert natural gas or methane from mild coal gasification products to a liquid fuel that is readily transported.

BACKGROUND INFORMATION

The purpose of this project is to develop a novel process by which natural gas or methane from coal gasification products can be converted to a transportable liquid fuel. It is proposed that methanol can be produced by the direct, partial oxidation of methane utilizing air or oxygen. It is anticipated that, compared to present technologies, the new process might offer significant economic advantages with respect to capital investment and methane feedstock purity requirements.

Methanol is presently manufactured by the catalytic reaction of synthesis gas (carbon monoxide and hydrogen) made by steam reforming of natural gas or heavier hydrocarbon fraction; several different, but related, processes exist (Danner 1970). Such two-step transformations require moderately high operating temperatures and pressures, reasonably pure feedstock, and are energy intensive. The present research effort attempts to avoid these requirements.

In the present research, the direct partial oxidation of methane to methanol utilizing air or oxygen is being studied. Methanol meets the requirements of improved transportability, can be utilized directly as a fuel, or can be transformed into long chain hydrocarbons via processes such as the Mobil MTG process. The overall transformation can be represented by reaction (1)

$$CH_4 + 1/2\ O_2 \dashrightarrow CH_3OH \qquad (1)$$

The essence of the project is to control the partial oxidation of methane to produce useful yields of methanol. It is crucial that complete oxidation to the thermodynamically stable products, carbon dioxide and water, be avoided. Methanol has been obtained as a major product in the partial oxidation of methane at high pressure and temperatures (Gesser 1985; Luckett 1976; Newitt 1934; Newitt 1932; Mantashyan 1981). The further oxidation products CH_2O, CO, and CO_2 accounted for the remainder of the methane consumed.

PROJECT DESCRIPTION

Our research approach is to achieve an economically attractive yield of methanol by developing and employing techniques to control the methane partial oxidation process. The application of control must arise from an understanding of the complex chemistry involved. It is based on exact control of the reaction kinetics of the direct oxidation of methane with termination of the reaction prior to reaching thermodynamic equilibrium to provide a high yield of methanol in a single step. The approach involves a homogeneous, gas-phase partial oxidation; it is non-catalytic. One focus of the project is a computer kinetic model describing all of the important free radical reactions. This model has no free parameters of fitting factors, only the rate constants for each of the individual reactions. The kinetic model has been improved and validated by extensive experimental efforts and is now used to guide the laboratory work.

An early approach which was investigated to control the partial oxidation process involved unconventional initiation of the chain reaction by laser irradiation or a plasma source. Subsequent work demonstrated that more effective control could be effected by conducting the process at high temperatures and abruptly terminating the reaction before over-oxidation occurred.

It was recognized early on that terminating the high temperature oxidation process at the precise moment would be both crucial and challenging. Several approaches to producing an exactly timed, precipitous drop of several hundred degrees Kelvin in the temperature of the reaction were conceived: (a) supersonic expansion through a nozzle, (b) impinging the hot reaction stream with a cooled jet spray, and (c) piston/cylinder compression and expansion. Conducting the partial oxidation under supercritical fluid conditions and quenching the process by rapid condensation was also considered. All of these approaches possessed the potential to produce rapid temperature changes which, in turn, would influence the populations of the various transient free radicals, the control of which was essential to the success of the process.

It was also recognized that complete methane conversion to methanol and other partially oxidized products could not be achieved in a single reaction stage and that economic success would depend on minimizing the number of recycling steps required. Several concepts were considered to address the recycle problem. (a) If cooling by means of supersonic expansion was adapted as discussed above, several steps of reaction/expansion could conceivably be achieved without the necessity of recompressing the reaction mix. Alternatively, (b) a single-stage process might be tenable if the methanol process operated on, e.g., a sidestream of a natural gas transportation pipeline. Converting 10-15% of the natural gas to methanol in a single stage process and reinserting the unreacted gas and reaction by-products back into the pipeline could be an economically attractive means to upgrade a portion of the natural gas.

Consideration was also given to the possibility of combining the partial oxidation process with a catalytic method to upgrade the oxidation product mixture. In particular, several experiments utilizing the Mobil ZSM-5 zeolite catalyst were conducted successfully to convert the methanol product to a hydrocarbon mixture resembling gasoline. It was envisioned that additional, non-methanol products, from the oxidation process might also be successfully upgraded with the proper choice of catalyst and conditions. Use of a Lunsford-type catalyst to generate methyl free radicals to seed the oxidation process was also considered.

An important point to make is that the methane partial oxidation approach undertaken in this research project lends itself to a variety of avenues to economically useful products. The approach taken was to focus on attempting to maximize the methanol yield by conducting high pressure, high temperature process runs with quenching of the reaction by expansion through a supersonic nozzle.

RESULTS

During the course of the research effort, we have employed an integrated, multidisciplinary approach using state-of-the-art theoretical and experimental tools including computer kinetic modeling, fundamental kinetics measurements, theoretical rate constant calculations, bench-scale reactor experiments, and systems analysis. We have made significant advances in understanding the detailed chemistry of the reactive intermediates and of the possible reaction pathways under various conditions and have been able to specify the reaction parameters necessary to obtain high yields of methanol.

Major accomplishments to date include the following:

- Demonstrated scientific proof-of-principle by achieving high selectivity for methanol formation for methane rich CH_4/O_2 mixtures.
- Developed a comprehensive kinetic working model with predictive capabilities and identified key reactions and reaction intermediates.
- Measured removal rate constants for methoxy radical interacting with O_2, CH_4, and a variety of unreactive gases over a wide temperature range.
- Developed a general procedure based on RRKM theory for calculation of rate constants of unimolecular reactions at high temperatures and pressures.
- Benchmarked the computer kinetic model against real experiments in a microprocessor controlled bench-scale static reactor.
- Predicted experimental conditions for high methane conversion (>25%) and high methanol selectivity (>50%) for single-pass conditions.
- Designed a high-temperature, high-pressure prototype of a pulsed-flow reactor based on results of hydrodynamic calculations.
- Fabricated, assembled, and began testing the bench-scale prototype reactor.
- Initiated discussions of collaboration and technology transfer with several U.S. companies.

A key accomplishment in the project has been the identification of experimental parameters to achieve high methane conversion while maintaining a high methanol selectivity. An extensive series of simulations was carried out for process conditions of 60 atmospheres with 25% initial oxygen, both at fixed (isothermal) temperatures and at various initial (adiabatic) temperatures. Some of the results shown in Figure 1. Also shown in Figure 1 are 8, 10, and 12% yield contours; we consider a single pass yield of 8-9% to be a minimum acceptable for an industrial process. The 1000 K isothermal simulation is very encouraging with a peak yield of 14.1% achieved at 29.9% methane conversion with a methanol selectivity of 47.3%. At slightly lower methane conversion (25%), the methanol selectivity is 51.6% for a predicted yield of 12.9%. Numerous other simulations were performed to determine the sensitivity of the overall yield to variations in pressure, temperature, methane/oxygen ratios, isothermal versus adiabatic conditions, added nitrogen, and seeding with a source of methyl free radicals.

Although the projected methanol conversion/selectivity per pass depicted in Figure 1 was most encouraging, as discussed above, it was known that it would be difficult to achieve an essentially isothermal reaction of a flammable methane/oxygen mixture at 1000 K with rapid quenching prior to complete oxidation. From the various potentially applicable approaches to quench the oxidation process discussed above, it was decided that an adaptation of supersonic nozzle flow and expansion might provide the necessary technology. However, the funding available for the project would not allow the design and construction of such a supersonic reactor. Instead, it was deemed desirable to demonstrate the validity of the model predictions at some yield value sufficiently removed from all previously reported efforts to engender interest from potential sponsors. For that purpose we envisioned a turbulent fast-flow reactor with free-jet expansion quenching at the end. Because the flow tube would not be isothermal, we wanted to achieve the highest yield possible prior to combustion. This required an allowance for a temperature rise of several hundred degrees before the expansion quenching. An adiabatic

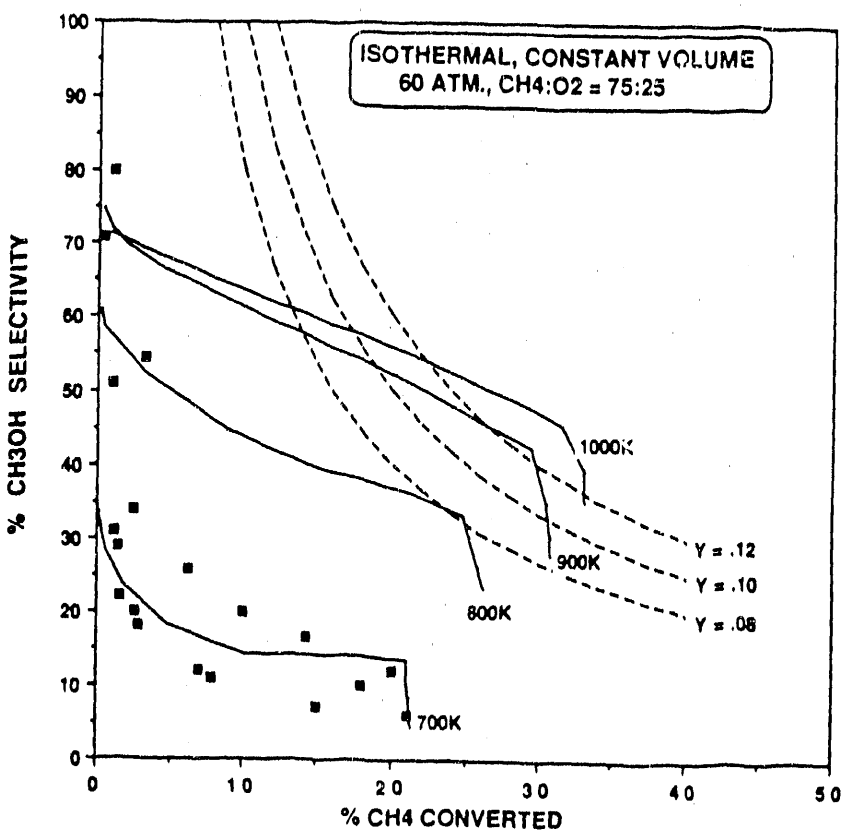

Figure 1. Kinetic model simulation of percent methanol selectivity versus percent methanol conversion at 1000 K, 800 K, and 700 K for CH_4/O_2 = 75/25 at 60 atmospheres. The blackened squares are assorted literature data.

simulation with an initial temperature of 850 K predicted that a yield of 8.3% with a 14.3% methane conversion and a methanol selectivity of 58% can be achieved when the temperature has risen to 1266 K. Quenching must then be achieved on a millisecond time scale to prevent combustion.

Based on the results of the kinetic modeling described above and additional hydrodynamic model calculations, the design, construction, and assembly of a turbulent, pulsed-flow, bench-scale reactor was completed during FY89. A schematic of the reactor design is shown in Figure 2. In this design, a 1-2 second duration pulse of high-pressure methane flows through a high-temperature reactor tube. During this transient methane flow, a pulse of oxygen is injected from a center-positioned coaxial tube. The partial oxidation chemistry that produces methanol occurs during residence in the tube and is subsequently quenched as the reaction mixture is expanded through the supersonic nozzle into a low-pressure "dump" tank. The reacted gases in the dump tank are analyzed using mass spectrometric and gas chromatographic techniques and real-time observation of the nozzle expansion cooling event is accomplished by a laser Schlieren imaging technique viewed remotely with a closed circuit television camera.

The methane and oxygen are introduced from separate preheated ballast tanks with solenoid-operated valves. The anticipated process conditions for this reactor are in the range 20-100 atmospheres and 800-1000 K. The residence time of the reacting gases at process conditions in the tube is approximately 10-200 ms. The sizes of ballast tanks, tubing, valves, the supersonic nozzle orifice, etc., depend upon the parameters of pressure, temperature, pulse length, and throughput, and are based on a set of computer-generated relationships for the operating parameters and conditions of the reactor. Transient temperatures and pressures throughout the reactor tube are measured with fast-response thermocouples and pressure transducers. The timed operations of the valves and data logging of pressures and temperatures is computer-controlled using LabVIEW (National Instruments, Inc.) software on a Macintosh II personal computer equipped with a multi-channel 12-bit analog-to-digital converter. This computer is also used for data reduction, analysis, and display.

The deceptively simple schematic design shown in Figure 2 turned out to be exceedingly difficult to implement. It was much more challenging than originally anticipated to conduct millisecond-scale experiments at 1000 K and 50-

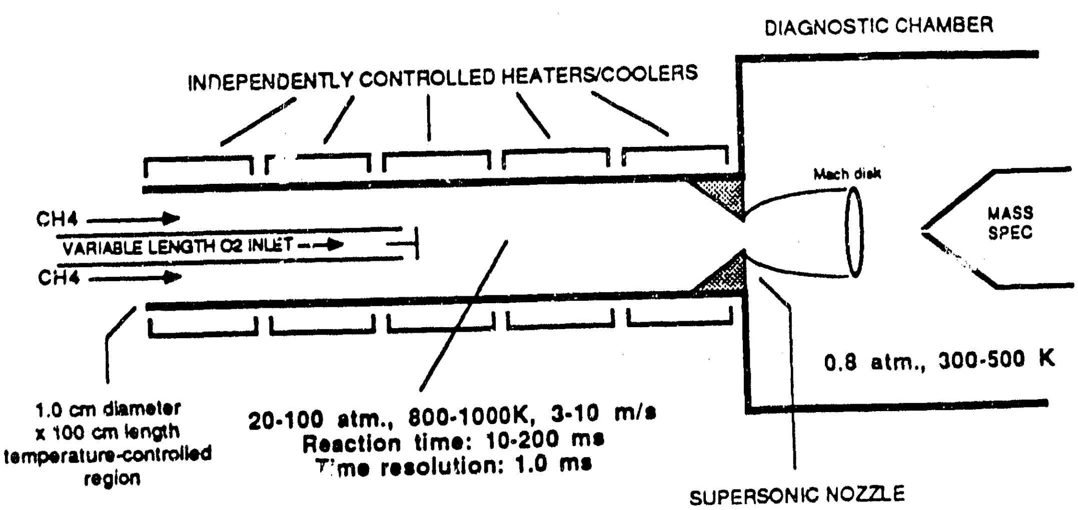

Figure 2. Schematic of reaction tube of pulsed, high-pressure flow reactor.

100 atmospheres pressure with a potentially explosive gas mixture. Numerous successful design and construction changes were made to the apparatus after problems were identified. All major modifications have now been completed and experiments have been initiated to at least partially validate the kinetic model and verify the exciting prediction depicted in Figure 1.

FUTURE WORK

During FY91, experiments will be performed in the prototype pulsed-flow reactor to partially validate the kinetic model and the prediction of high methanol selectivity at high methane conversion under high temperature/ pressure conditions. The results will also provide guidance for the design during FY92 of an advanced, supersonic, pulsed-flow reactor which will operate with a stoichiometric methane/oxygen mix within explosive limits. Concurrently during FY91, various options for increasing the conversion efficiency will be explored. These include, but are not limited to, (a) seeding the reaction with independently-generated free radicals, (b) using zeolite catalysts to convert and partial oxidation product mix to higher hydrocarbons, and (c) utilizing multistaging techniques. The various alternative catalytic and non-catalytic approaches discussed above will be systematically evaluated to determine the most appropriate approach to maximizing the yield of desired product(s).

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Suprabiotic Catalyst Systems for Selective Oxidation of Light Alkane Gases to Fuel Oxygenates

CONTRACT INFORMATION

Contract Number	DE-FC21-90MC26029
Contractor	Sun Refining and Marketing Company Research and Development Department P.O.Box 1135 Marcus Hook, PA 19061 (215)-447-1731
Contractor Project Manager	James E. Lyons
Principal Investigator	James E. Lyons
METC Project Manager	Rodney D. Malone
Period of Performance	January 1, 1990 to September 30, 1990

Schedule and Milestones

	J F M A M J J A S
Perhaloporphyrin Complexes	
- Synthesis of $M(TPPF_{20}\text{-}\beta\text{-}Br_8)X$ (16 complexes in 1990)	------------------------------------ (12 complexes made in 9 mo.)
- Characterize Complexes	------------------------------------
- Test Complexes for Alkane Ox. ($i\text{-}C_4$, C_3, C_2, C_1, Natural Gas)*	------------------------------------ (all catalysts tested)
(all catalysts remained in the program as long as they were active)	
Polyoxoanion Complexes	
- Synthesis of $H_7[PW_9M_3O_{37}]$ (9 complexes in 1990)	------------------------------------ (9 complexes made in 9 mo.)
- Characterize Complexes	------------------------------------
- Test Complexes for Alkane Ox. ($i\text{-}C_4$, C_3, C_2, C_1, Natural gas)	------------------------------------ (all catalysts tested)
(all catalysts remained in the program as long as they were active)	
Framework Substitued Zeolites	
- Synthesized [M]Zeol Complexes (6 catalysts in 1990)	------------------------------------ (4 catalysts made in 9 mo.)
- Characterize Catalysts	------------------------------------
- Test Catalysts for Alkane Ox.) (Methane, Natural Gas)	------------------------------------ (catalysts tested for methane)

OBJECTIVES

The objective of the work presented in this paper is to develop new, efficient catalysts for the selective transformation of the light alkanes in natural gas to alcohols for use as liquid transportation fuels, fuel precursors and chemical products. There currently exists no DIRECT one-step catalytic air-oxidation process to convert these substrates to alcohols. Such a one-step route would represent superior useful technology for the utilization of natural gas and similar refinery-derived light hydrocarbon streams. Processes for converting natural gas or its components (methane, ethane, propane, and the butanes) to alcohols for use as motor fuels, fuel additives or fuel precursors will not only *add a valuable alternative to crude oil but will produce a clean-burning, high octane alternative to conventional gasoline.*

BACKGROUND INFORMATION

We have devised a new catalytic approach to the direct production of alcohols from light alkanes which grew out of the recognition that metal oxo complexes like those that are intermediates of enzymatic alkane hydroxylations might be generated directly from reaction of air or oxygen with metals in certain supportive molecular environments. To date, the enzymatic systems are the only relatively efficient catalysts for the conversion of light alkanes to alcohols. Synthetic systems which mimic the enzymes have also had some limited success in this area. Biological and biomimetic oxidations, however have the requirement of very speciallized and expensive co-reductants which are stoichiometrically consumed during reaction. The catalysts which are the subject of this study are designed to directly activate molecular oxygen and catalyze the oxidation of light alkanes to alcohols using ONLY molecular oxygen without the need for co-reductants which limit the commercial potential of the chemistry. We have used these catalysts to oxidize light alkanes directly by reaction with air or oxygen and find that they are able to convert light alkanes to alcohols under relatively mild conditions.

PROJECT DESCRIPTION

This project is an experimental approach to the design, synthesis, characterization and testing of oxidation-active transition metal centers for cleaving the dioxygen molecule and producing metal oxo intermediates which react with alkanes to convert them to alcohols. The molecular environment in which the oxidation-active metal center is located is critical in generating active catalysts. It must tune the center electronically to access appropriate oxidation states and should enable two metal centers to participate in the oxygen splitting process. We are investigating three molecular environments which could be hospitable ones for the active species that we are trying to generate: a) perhaloporphyrin, perhalophthalocyanine or related macrocycles, b) polyoxometallates and c) regular oxidic lattices such as zeolites and related structures. We are testing these three sets of catalysts for activity in the mild oxidation of light alkanes (isobutane, propane, ethane and methane).

RESULTS AND ACCOMPLISHMENTS

OXIDATIONS CATALYZED BY PERHALOPORPHYRINS

Direct catalytic conversion of alkanes to alcohols using molecular oxygen as the oxidant is of great interest as a means of converting these available and inexpensive hydrocarbons to valuable products(1) Porphyrinatoiron complexes are known to catalyze the biomimetic hydroxylation of alkanes using as oxidants oxygen atom transfer reagents such as iodosylbenzene (2-5), hypohalites (6,7) and hydroperoxides (8,9). Oxygen has been used as the oxidant together with electrons supplied by co-reductant systems. An iron porphyrin complex has been shown to catalyze the oxidation of cyclohexane to cyclohexanone using oxygen as oxidant, zinc amalgam as co-reductant, methyl viologen for electron transfer and acetic anhydride as an acylating agent (10). Recently, alkane hydroxylation with O_2 has produced alcohols electrochemically (11). The need for expensive co-reductants or oxygen atom transfer reagents imposes an economic disadvantage on commercial or large scale synthetic application of this chemistry.

In recent publications (12-15) we have described a series of metalloporphyrin complexes that efficiently catalyze the oxidation of light alkanes with oxygen or air under mild conditions without the need for added co-reductants or oxygen atom transfer reagents. During the course of this work we found that halogenation of the porphyrin ring of porphyrinatometal(III) complexes greatly increased their catalytic activity for the selective mild reactions of alkanes with molecular oxygen (13-15). Furthermore the greater the halogen content in the porphyrin ring, the greater was the catalytic activity of the complex (16-18).

In this paper we describe the first series of metalloperhaloporphyrin complexes which have been used for air-oxidation of light alkanes and how perhalogenation tunes the redox potential of these complexes for high oxidation activity.

We have found that when an oxidation-active first row transition metal such as iron(III), manganese(III) or chromium(III) is placed in the coordination sphere of the perhaloporphyrin: <u>tetrakis</u>pentafluorophenyl-β-octabromoporphyrin, $TPPF_{20}$-β-Br_8, it becomes several orders of magnitude more active for alkane oxidation than the same metal in a non-halogenated macrocycle. This enables us to oxidize light alkanes at temperatures far lower than is usually possible with conventional catalysts resulting in greater selectivity to partial oxidation products such as alcohols. Tables 1,2 show that isobutane and propane are oxidized much more rapidly in the presence of the $TPPF_{20}$-β-Br_8 complexes than either unhalogenated complexes or than partially halogenated complexes. Another benefit of halogen in the macrocycle is that it lends stability to the catalyst resulting in longer life.

The iron complexes of the perhalo (TPPF20-β-Br_8) ligand system are far and away the most active of the three metal sets which we have investigated. The complex is by far the most active liquid phase light alkane air-oxidation catalyst yet known. Table 3 shows that neat isobutane can be oxidized to <u>tert</u>-butyl alcohol with unprecedented rates and high (90-95%) selectivities at very mild temperatures. Room temperature oxidation of isobutane can give over 90% selectivity to TBA at 20% conversion and over 12,000 catalytic turnovers. Inspection of the UV/VIS spectrum of the resulting complex shows that the porphyrin ligand system of the catalyst is virtually unchanged at this point.

TABLE 1. ISOBUTANE OXIDATIONS USING $(TPPF_{20}\text{-}\beta\text{-}Br_8)Fe(III)$ CATALYSTS[a]

	mmoles	T,°C	t, Hr.	TBA T.O.[b]	Sel. %[c]
FE(TPP)Cl	0.025	60	6	0	-
$Fe(TPPF_{20})N_3$	0.016	60	6	1050	88
		40	6	470	89
		27	6	54	95
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_4)OH$	0.013	60	6	1220	86
		40	6	360	90
		26	6	70	91
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)Br$	0.013	60	6	1490	87
		40	6	470	89
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)Cl$	0.013	60	6	1860	91
		40	6	690	90
		27	6	130	90
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)N_3$	0.013	60	6	1550	87
		40	6	670	89
		25	6	620	na

a A solution of the catalyst in 25 ml benzene containing 6 grams of isobutane was stirred at the designated temperature under 100 psig of O_2 for the designated time.

b Moles O_2 consumed/mole catalyst used.

c (Moles t-butyl alcohol produced/total moles liquid product) X 100.

TABLE 2. PROPANE OXIDATIONS USING FIRST ROW METAL COMPLEXES OF $TPPF_{20}\text{-}\beta\text{-}Br_8$ AS CATALYSTS[a]

	Time Hours	T,°C	T.O.[B]	IPA Acetone[c]
$Fe(TPPF_{20})N_3$	4.5	125	370	0.8
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)Cl$	4.5	125	420	1.0
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)N_3$	4.5	125	514	0.9
$Cr(TPPF_{20})Cl$	4.5	125	0	-
$Cr(TPPF_{20})N_3$	4.5	125	41	< 0.1
$Cr(TPPF_{20}\text{-}\beta\text{-}Br_8)Cl$	4.5	125	111	0.3
$Cr(TPPF_{20}\text{-}\beta\text{-}Br_8)N_3$	4.5	125	87	0.6
$Mn(TPPF_{20})N_3$	3	125	0	-
$Mn(TPPF_{20}\text{-}\beta\text{-}Br_8)N_3$	4.5	125	51	1.0

a Propane (1.36 mol) was added to benzene (48 ml) containing the catalyst (0.013 mmol). The solution was stirred for 3 hrs. at 125ρc under 1000 psig of air in a glass lined autoclave. Liquids and gases were analyzed by g.c. production of carbon oxides never amounted to 10% of total products. Isopropyl alcohol and acetone exceeded 90 mole % of carbon-containing reaction products in all cases.

b Moles of acetone plus isopropyl alcohol formed per mole of catalyst used.

c Molar ratio of isopropyl alcohol to acetone formed.

d Reactions runs in acetonitrile rather than benzene.

TABLE 3

IRON HALOPORPHYRIN-CATALYZED ISOBUTANE OXIDATIONS[a]

Catalyst	T, C	Charge to Reactor: t, Hrs.	Charge to Reactor: $i\text{-}C_4H_{10}$	O_2	Reaction Products, mmoles: TBA	Reaction Products, mmoles: Acetone	Reaction Products, mmoles: CO_2	Reaction Products, mmoles: CO	Conversion $i\text{-}C_4H_{10}$,%	Select. TBA,%[b]	TON[c]
$Fe(TPPF_{20}\text{-}\beta\text{-}Br_8)Cl$	80	3	1870	53	277	43	23	8.0	17	87	10,660
	80	3	1862	100	429	86	26	4.9	28	83	17,150
	80	3	1862	148	414	81	28	6.0	27	84	16,500
	80	3	1869	205	290	45	37	10.5	18	87	11,180
	60	3	1865	47	230	23	20	tr	14	91	8,420
	60	3	1874	139	184	18	17	tr	11	91	6,730
	25	71.5	[illegible]	53	372	35	27	tr	22	92	13,560
$Fe(TPPF_{20})OH$	24	143	1871	53	332	17	18	0	18	95	12,150

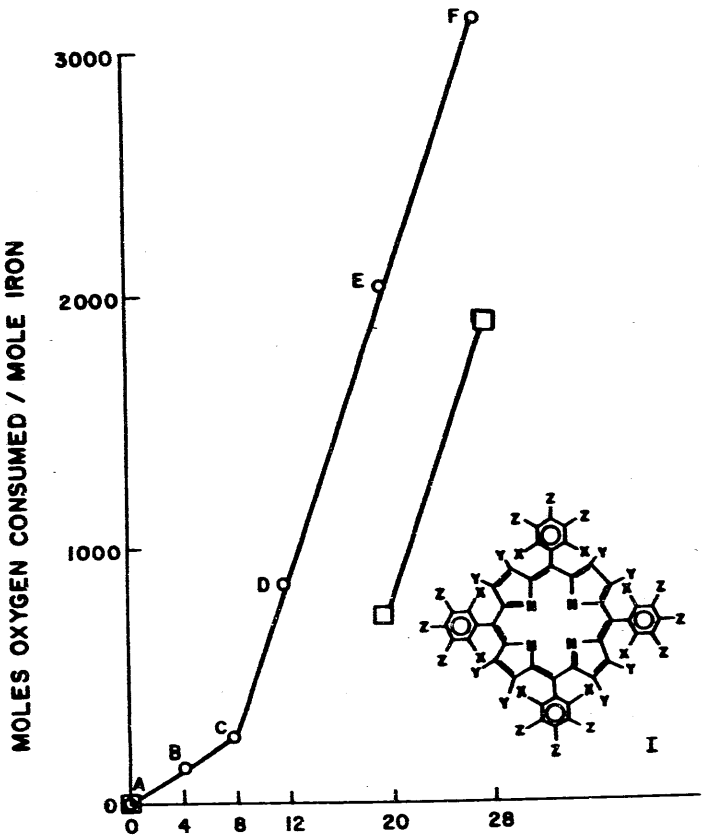
a Isobutane was oxidized by an oxygen-containing gas mixture (75 atm, diluent = N_2) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

b (moles TBA/moles liquid product) X 100.

c moles (TBA + Acetone) produced/mole catalyst used.

FIGURE 1.

CATALYST ACTIVITY VS. # OF HALOGENS



LIGAND, I	X	Y	Z
A (TPP)	8H	8H	12H
B (TPPβ-Br_4)	8H	4H,4Br	12H
C ($TPPCl_8$)	8Cl	8H	12H
D ($TPPCl_8$ β-Br_4)	8Cl	4H,4Br	12H
E ($TPPF_{20}$)	8F	8H	12F
F ($TPPF_{20}$ β-Br_8)	8F	8Br	12F

CATALYST ACTIVITY VS. REDOX POTENTIAL
(ISOBUTANE OXIDATION AT 80°C)

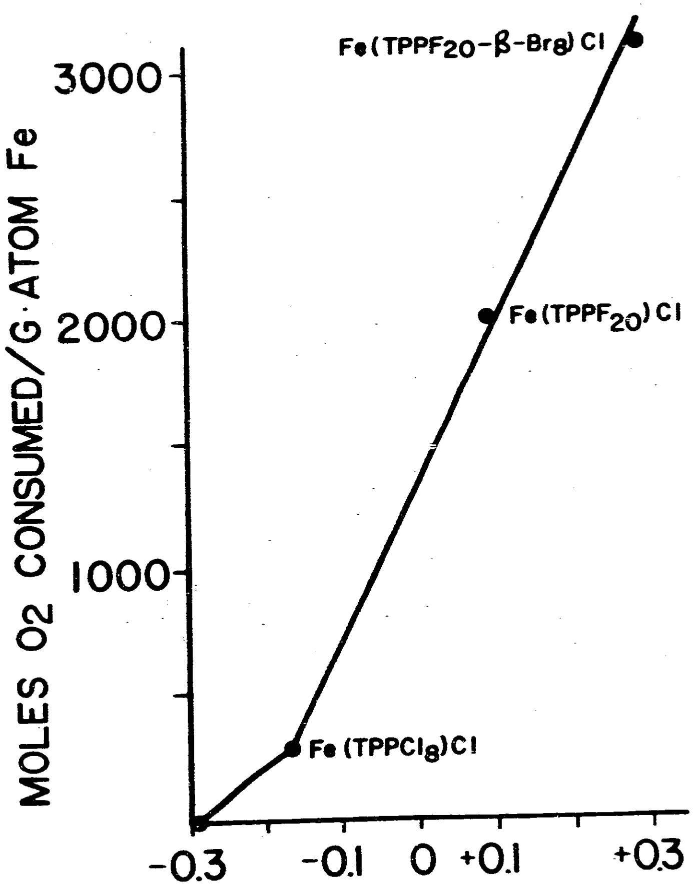


FIGURE 2

We are beginning to understand the mechanism of this activity and are able to correlate it quantitatively with the reduction potential at the central metal atom. Figure 1 shows a steady increase in catalytic activity with the extent of halogenation which is nearly exactly matched by a corresponding increase in reduction potential at the iron center, Fig 2. It is possible that the oxidation occurs via the pathway shown in Figure 3. As electron density is removed from the iron center the position of equilibrium (a) is shifted away from Fe(III)(O_2) to Fe(II) which allows enough Fe(II) to survive to bind the other end of the oxygen molecule, (b). Cleavage of the ferric peroxide (c) gives the iron oxo complex which can hydroxylate the alkane (d). The position of equilibrium (f) allows a standing concentration of the active intermediates Fe(II) and Fe(IV)O to exist in the presence of the diiron μ-oxo complex which is usually inactive and is formed irreversibly. In-situ spectroscopy supports this contention as we can observe the Fe(II) and the Fe(III)OFe(III) intermediates during reaction. Furthermore [(TPPF$_{20}$-β-Br$_8$)Fe(III)]$_2$O is an active catalyst and can be recovered from the reaction mixture regardless of what TPPF$_{20}$-β-Br$_8$ iron complex is used as the catalyst.

The dependence of oxidation activity on extent of halogenation in these systems suggests that severe electron withdrawal from the iron center leads to an increase in reduction potential and an increase in the reaction rate. Added electron withdrawal should continue this trend and even more active catalysts will be discovered. The importance of this finding is that continued work could lead to a route from the C_4 hydrocarbons present in natural gas to the valuable high octane fuel component - tert-butyl alcohol. In addition, this alcohol is also the precursor to the most widely used C_4 oxygenate in motor fuel today - MTBE.[4]

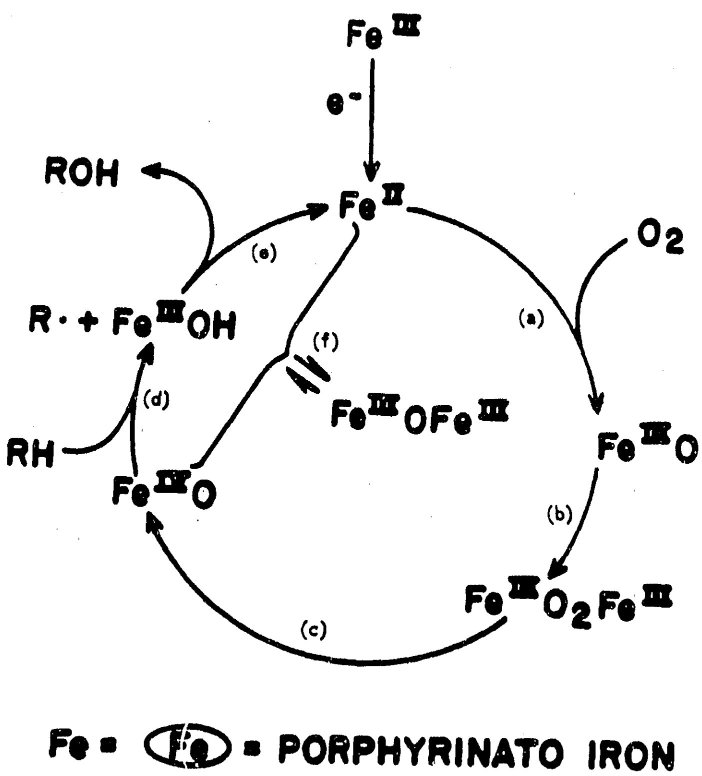


FIGURE 3

OXIDATIONS CATALYZED BY POLYOXOANIONS

Despite their relatively high stability, the first generation perhalogenated metal catalysts are still not stable enough to survive the higher temperatures required to oxidize propane, ethane and methane for long periods of time. Thus we are using polyoxometallates such as Keggin ions, $M_x[PM_{12}O_{37-40}]$ as more rugged molecular environments for oxidation-active metals. Another advantage of the Keggin structures is that we have been able to incorporate more than one oxidation-active metal center in the Keggin structures in such a way that the metals are proximate to one another (19-24). We reasoned that this could be important in splitting the oxygen molecule through structures like those which may form via a reaction similar to step c in Figure 3. We were able to synthesize a large number of Keggin structures having three-metal clusters as shown in Figure 4. In addition to having good isobutane oxidation activity, these complexes were quite active for oxidizing propane and even showed some activity for methane and ethane oxidation, Table 4, although rate and selectivity were poor (conversion < 5%, selectivity < 33%). It is still questionable whether two metals in proximity within a polyoxometallate can cooperate effectively to split an oxygen molecule to give the desired active metal oxo without causing the Keggin structure to rupture. We are now studying complexes which have oxidation active metal ions BOTH in the framework AND in the exchange positions and are testing these catalysts. Cooperativity between exchange and framework irons may give catalysts with even greater activity.

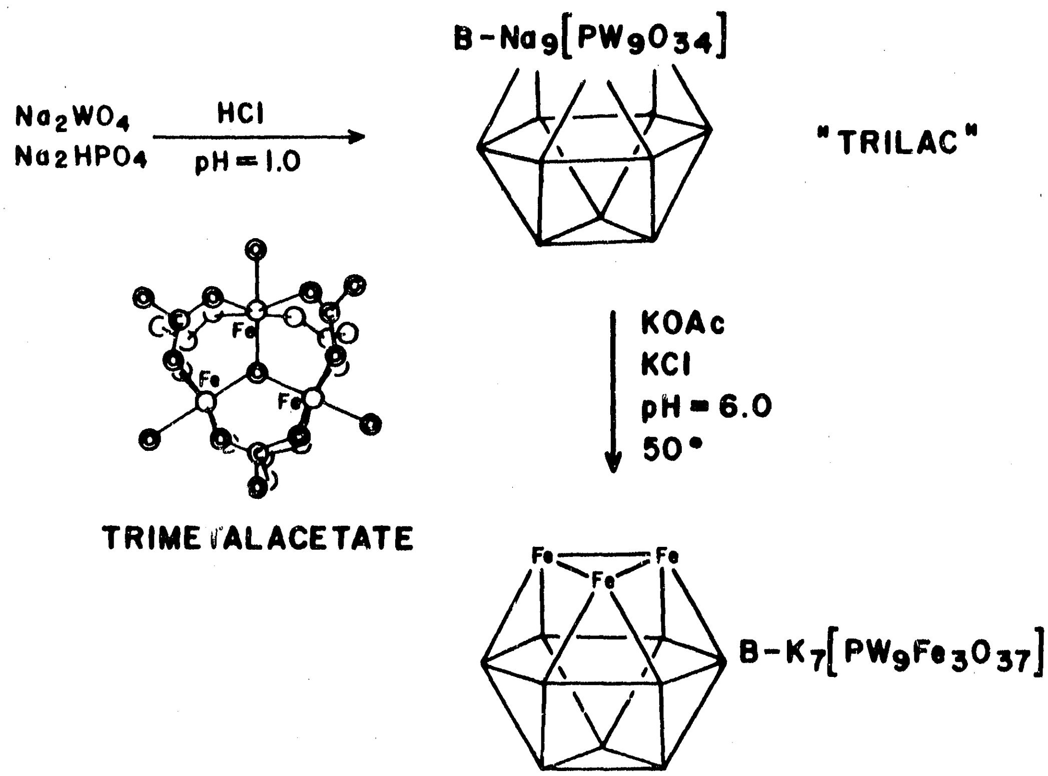


FIGURE 4

TABLE 4. OXIDATION OF ALKANES USING HETEROPOLYACID CATALYSTS[a]

SUBSTRATE	CATALYST	T,°C	T.O'S[a]	IPA/A[c]
Propane	None	150	0	-
	$H_3PW_{12}O_{40}$	150	750	0.85
	$H_6PW_9Fe_3O_{37}$	150	2240	0.65
	$H_6PW_9Fe_3O_{37}\bullet NaN_3$	150	8110	0.61
	$H_4PO_{11}FeO_{39}\bullet NaN_3$	150	2034	0.52
	$Fe_3O(OAc)_6(OH)_3$[c]	150	20	na
	$Fe_3O(OAc)_6(OH)_3$[c]$\bullet NaN_3$	150	190	0.53
	$H_7PW_9FE_2NiO_{37}\bullet NaN_3$	150	9730	0.71
	$H_7PW_9Fe_2ZnO_{37}\bullet NaN_3$	150	5640	0.65
	$H_7PW_9Fe_2MnO_{37}\bullet NaN_3$	150	5570	0.65
	$H_7PO_9Fe_2CoO_{37}\bullet NaN_3$	150	3290	0.70
	$H_6PW_9Cr_3O_{37}$	150	4420	0.47
	$H_6PW_9Cr_3O_{37}\bullet NaN_3$	150	5550	0.52
Ethane	$H_7PW_9Fe_2NiO_{37}$	200	240	
Methane	$H_6PW_9Fe_3O_{37}$	280	50	

a Moles propane/mole catalyst used.

b Propane, 1.36 moles was added to a solution of 5μ moles catlayst in 38 ml acetonitrile and heated under 1000 psig air for 3 hrs.

c 44μ mole catalyst used.

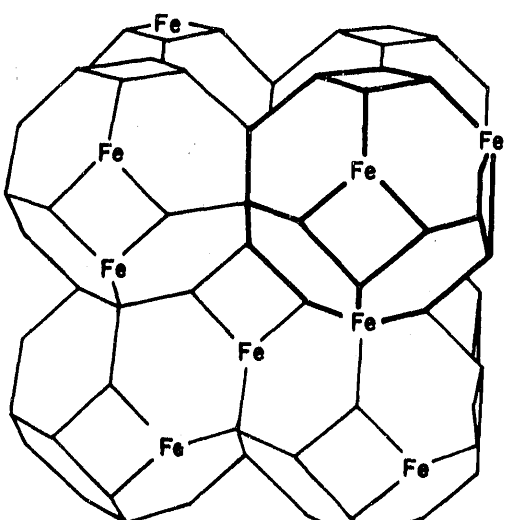
TABLE 5. VAPOR PHASE AIR OXIDATIONS OF METHANE TO METHANOL

CATALYST	GHSV h^{-1}	Bed T °C	CH_3OH Sel., %	CH_4 Conv., %	O_2 Conv., %
[Fe]SOD	530	407	64	4.6	76
		461	70	5.7	90
		418	68	5.4	91
		422	65	5.4	92
		432	63	5.5	90
		442	64	6.1	90
Hydroxysodalite	530	404	-	0.0	0
		430	9	0.3	4
		445	24	5.1	84
Fe_xO_y/SiO_2 (10-15%)	530	431	26	5.1	85
	700	398	10	0.5	11
		409	18	1.2	16
		420	20	2.7	74
		428	23	3.9	83
[Fe] ZEOL	700	400	33	2.4	52
		430	34	3.8	74

a P=800 psig, 3:1 methan:air. Quartz lined reactor with by-pass open.

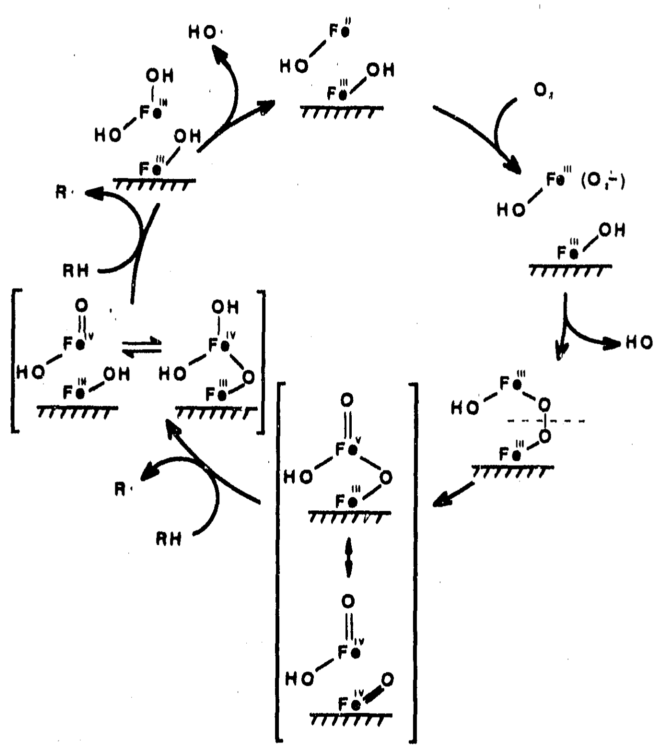
OXIDATIONS CATALYZED BY ZEOLITES

Using metals in perhalogenated macrocycles or in polyoxometallates, we have activated all of the light (C_1-C_4) alkanes with varying degrees of success in the liquid phase. Since it may be desirable to operate in the vapor phase, especially with methane or natural gas, we have implanted oxidation-active metals into the framework of zeolitic matrices and onto other regular oxidic surfaces and examined their activity for the vapor phase oxidation of light alkanes with an emphasis on methane oxidation to methanol. Again, metal centers which can achieve high oxidation states and which can operate cooperatively with nearby oxidation-active metal centers to possibly cleave the dioxygen molecule are the most active. Table 5, for example shows the results of the oxidation of methane using an iron sodalite catalyst, Fig. 5, which is synthesized so that it has both exchange and framework iron atoms in close proximity (25). A catalyst having only framework irons is not nearly as active as one having both types of iron sites, even though the framework irons are proximate. A hypothetical mechanism is suggested to rationallize these results, Fig. 6, although other possibilities certainly exist.



5.

Although it is believed that high oxidation state iron oxo species are capable of homolytically cleaving carbon-hydrogen bonds, low temperature reactions in the liquid phase may produce alcohols directly by collapse of the metal-bound radicals as shown in Figure 3, step e. As we indicate in Fig. 6, it would be expected that a significant fraction of the bound radicals formed at elevated temperatures would be expelled into the gas phase where they would react by homogeneous vapor phase pathways. In order to assess the fate of gas phase radicals in such a process, we have modelled this reaction kinetically. We have found that methanol selectivities above 60% can be achieved by gas phase conversion of methyl radicals. It is uncertain as yet how high the methanol selectivity can go as the methyl radical flux is increased by surface catalysis. Kinetic analysis tells us, however, that a large fraction of even those radicals which escape the coordination sphere of the metal center on which they are generated will give rise to methanol.



6.

CONCULSIONS

In conclusion, it appears that catalysts can now be designed, synthesized and utlilized which have sufficient activity for cleaving the C-H bonds of even the most refractory components of natural gas - methane and ethane. Further development of these catalysts may provide the first efficient production of methanol from methane under mild conditions in either the liquid or vapor phase. In the short term, direct conversion of isobutane to valuable fuel components may be realized.

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Catalytic Assessment of Methane Conversion to Liquid Fuels

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BACKGROUND INFORMATION

The overall objective of this research project is to identify and develop economically efficient processes for the conversion of natural gas to liquid fuels. Methane is the major component of natural gas; therefore, the specific objectives are (1) to prepare and test new methane conversion catalysts, (2) to conduct fundamental catalyst characterization studies in an effort to elucidate the overall reaction mechanism for methane conversion and (3) to explore and develop novel concepts for the conversion of natural gas.

Natural gas, which consists primarily of methane, is one of our most abundant natural resources. Unfortunately, many of the natural gas reservoirs are located in relatively remote areas, and high transportation costs tend to prohibit extensive use of this resource. One solution to this problem is to develop processes that convert the natural gas, or methane, into higher value products and thus offset these high transport costs.

The conversion of methane to higher hydrocarbons or oxygenated materials still remains one of the most challenging problems in the field of catalytic research. The high molecular stability of methane (C-H bond strength = 104 kcal/mol) makes it difficult for any conversion to useful chemicals; however, recent advances in catalytic research have indicated that improved product yields can be obtained for some partial oxidations processes.

Formation of ethane and ethylene, oxidative dimerization

$$2\ CH_4 + (n/2)\ O_2 \ = \ C_2H_{8-2n} + n\ H_2O\ , \quad \text{(where n = 1 or 2)}$$

has shown the most promise.[1-3] A variety of catalytic materials have been identified that are capable of giving product yields of approximately 20%. Unfortunately, reaction temperatures in excess of 700 °C are required to achieve these yields. Initial activation in all cases is most likely via hydrogen atom abstraction with the subsequent formation of a methyl radical. In certain instances, the presence of surface-generated gas phase methyl radicals has been demonstrated.[4,5] Here, it is likely that gas phase coupling of these species is the major route for selective product formation. Product distributions over most of the other oxidative dimerization catalysts examined are all similar, and it is entirely possible that this type of a hetero-geneous-homogeneous mechanism is also in effect over these materials. By operating in this manner, overall control of the reaction is transferred from the catalyst surface to the gas phase, and it is expected that the product yield will be limited according to high temperature gas phase kinetics.[6] In addition to this limitation, the high temperatures tend to volatilize the active catalyst components and thus deactivate the materials.

The catalytic formation of oxygenated materials, methanol,

$$CH_4 + 1/2\ O_2 \ = \ CH_3OH,$$

and formaldehyde,

$$CH_4 + O_2 = H_2CO + H_2O,$$

have also been extensively examined.[7] In these cases, lower temperatures are employed, but the overall yields are generally extremely low (on the order of 5%). Initial activation is once again by C-H bond cleavage but in this case it is more probable that subsequent steps of the reaction occur on the catalyst surface rather than in the gas phase.

The recent advances in the catalytic conversion of methane have been encouraging; however, there still remains room for significant improvement. At METC, a diversified research program has been designed to investigate the catalytic conversion of natural gas, in particular via the oxidative dimerization route. In addition to simply testing different catalyst compositions, a variety of fundamental studies are being simultaneously conducted in an attempt to (1) elucidate the overall reaction mechanism and (2) provide guidance for developing more effective catalytic materials. Considerable effort is also being directed towards identifying catalytic materials that operate at lower temperatures, thus eliminating the problems mentioned above.

EXPERIMENTAL

Catalyst preparation and experimental procedures have been described in considerable detail elsewhere;[8-11] therefore, only a brief summary of the more important aspects will be presented here. The perovskites were prepared either by a solid state technique[12] or a freeze-drying technique. Metals were doped into the catalysts by slurrying the appropriate alkali metal salt with the pure oxide in water. Generally, the materials were subjected to a high temperature pretreatment before use. The supported molten salt catalysts (SMSC) were prepared from metal salts, using the incipient wetness technique, after evacuation of the porous support. Catalysts were evaluated in either an alumina or a fused-quartz fixed-bed reactor (approximate dimensions: 235 mm length, 6.5 mm inside diameter (i.d.), 100 mm heated length) that was operated in the down-flow mode. Products were analyzed by conventional on-line gas chromatography techniques (TCD detector, Porapak Q and 5A molecular sieve columns). The formaldehyde was analyzed by means of an iodometric titration. On line mass spectrometry (MS) was employed to monitor oxygen loss during the temperature programmed desorption (TPD) experiments.

Surface areas and pore size distributions were obtained by volumetric methods using either nitrogen or krypton as the absorbate. Auger electron spectroscopy (AES) was performed using a Perkin Elmer SAM-590 system. X-ray photoelectron spectra (XPS) were recorded with a cylindrical mirror analyzer and a 15-kV X-ray source (Physical Electronics Division of Perkin Elmer). Scanning electron microscopy (SEM) experiments were conducted on an ETEC Autoscan.

RESULTS/ACCOMPLISHMENTS

Catalyst Evaluation

A number of new materials have been identified which are capable of promoting the catalytic conversion of methane to C_2 products. These include a variety of perovskite compounds and several pure and doped metal oxide materials. A complete list of all the materials examined is given in Table 1. Product yields of approximately 20% can be obtained over the active catalysts when reaction temperatures are in the range of 800 °C. In contrast to many of the earlier oxidative dimerization catalysts, these materials appear to be somewhat more stable under reaction conditions. For example, the perovskite materials showed no significant

Table 1. Materials Examined for Methane Conversion Activity

PEROVSKITES

$La_{0.6}Na_{0.4}MnO_3$*, $Gd_{0.9}Na_{0.1}MnO_3$*, $La_{0.9}Na_{0.1}MnO_3$*, $Sm_{0.9}Na_{0.1}MnO_3$*,

$Ho_{0.9}Na_{0.1}MnO_3$, $La_{0.9}K_{0.1}MnO_3$, $CaMnO_3$, $GdMnO_3$

DOPED-PEROVSKITES

$Na_4P_2O_7/CaMnO_3$, $Na_2CO_3/CaMnO_3$, $Na_4P_2O_7/GdMnO_3$*, $Na_2CO_3/GdMnO_3$,

$Na_2CO_3/Gd_{0.9}Na_{0.1}MnO_3$, $K_2CO_3/La_{0.9}K_{0.1}MnO_3$

OXIDES

La_2O_3, CaO, Gd_2O_3, manganese oxide, CaO-manganese oxide, Gd_2O_3-manganese oxide

DOPED-OXIDES

$Na_4P_2O_7/CaO$*, Na_2CO_3/CaO, $Na_4P_2O_7/Gd_2O_3$*, Na_2CO_3/Gd_2O_3,

$Na_4P_2O_7$/manganese oxide*, Na_2CO_3/manganese oxide, $Na_4P_2O_7/Gd_2O_3$-manganese oxide*, Na_2CO_3/Gd_2O_3-manganese oxide, $Na_4P_2O_7$/CaO-manganese oxide,

Na_2CO_3/CaO-manganese oxide

*Indicates an active and selective material with enhanced stability

deactivation even after 100 hours on stream. This stability may result from the solid state structure of these substances. In general, materials promoted with $Na_4P_2O_7$ showed stable behavior whereas the Na_2CO_3-promoted materials slowly deactivated. Additional details on this stabilizing effect will be presented in the following section.

Catalyst Characterization

A number of techniques have been used to obtain fundamental information about the catalyst structure. In this section, results from TPD, AES, and SEM are highlighted.

TPD studies were conducted on a series of the perovskite materials with the general formula $A_{1-x}B_xMnO_3$ (where A is Gd, Sm, La or Ho; B is Na or K; and x = 0 or 0.1), and the temperature at which maximum oxygen desorbed (T_{max}) was correlated with the C_2 selectivity. The TPD chromatograms for oxygen desorption are presented in Figure 1. Two types of oxygen are observed. The first type, α oxygen, desorbs over a wide range of temperatures (900-1,200 K), while the second type, β oxygen, starts appearing after 1,023 K. The values for T_{max}, corresponding to the maxima for α oxygen desorption, are plotted in Figure 2 along with the C_2 selectivities obtained over these materials. The plot shows that T_{max} for oxygen desorption correlates very well with the C_2 selectivity. The catalyst with oxygen desorbing at the highest temperature (strongly bound oxygen) showed the highest C_2 selectivity, while $LaMnO_3$, which

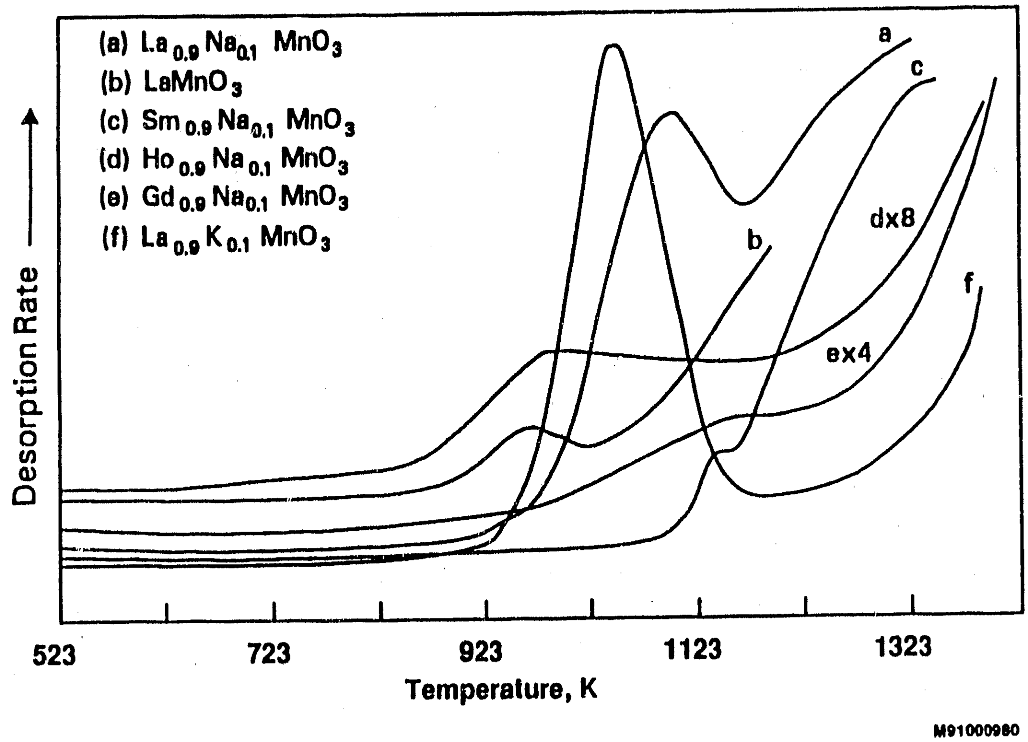

Figure 1. Temperature Programmed Desorption of Oxygen From Perovskite Type Catalysts (Heating Rate = 1 K/s; He Flow Rate = 0.5 cm^3/s; 0.25 g catalyst)

desorbs oxygen at the lowest temperature (weakly bound oxygen), is the least selective for the conversion of methane to C_2 products. This suggests that in the catalytic oxidation of methane to higher hydrocarbons one of the more important factors in determining product selectivity may be the binding energy of oxygen to the surface of the catalyst. With the exception of the methyl radical generator, effective dimerization catalysts must be composed of relatively inert oxygen species to eliminate production of non-selective surface CO_2.

It was previously mentioned that enhanced catalyst stability was generally obtained when $Na_4P_2O_7$, rather than Na_2CO_3, was used as the alkali metal dopant. For example, stable reactivity was maintained for 26 hours over $Na_4P_2O_7/CaO$, while a Na_2CO_3/CaO catalyst showed a continual decline over the same period. AES and SEM have been employed to shed some light on the reason for this difference in stability.

The results of the elemental analysis by AES on the above materials is presented in Table 2. After 4 hours of reaction, there was a sharp decrease in the amount of sodium on the surface of the $Na_4P_2O_7/CaO$ catalyst. This ratio is similar to that observed after 26 hours of

Table 2. Elemental Analysis by Auger Electron Spectroscopy of the Surfaces of Na-Doped CaO Catalysts Before and After Reaction at 1,101 K

Sample	Na/Ca	P/Ca
1. 0.1 $Na_4P_2O_7/CaO$		
• Before reaction	0.29	0.06
• After 3 hr reaction	0.14	
• After 26 hr reaction	0.10	0.05
• After 26 hr at 1,101 K without reactants	0.29	0.07
2. 0.1 Na_2CO_3/CaO		
• Before reaction	0.10	
• After 20 hr reaction	0.04 (some areas had zero)	

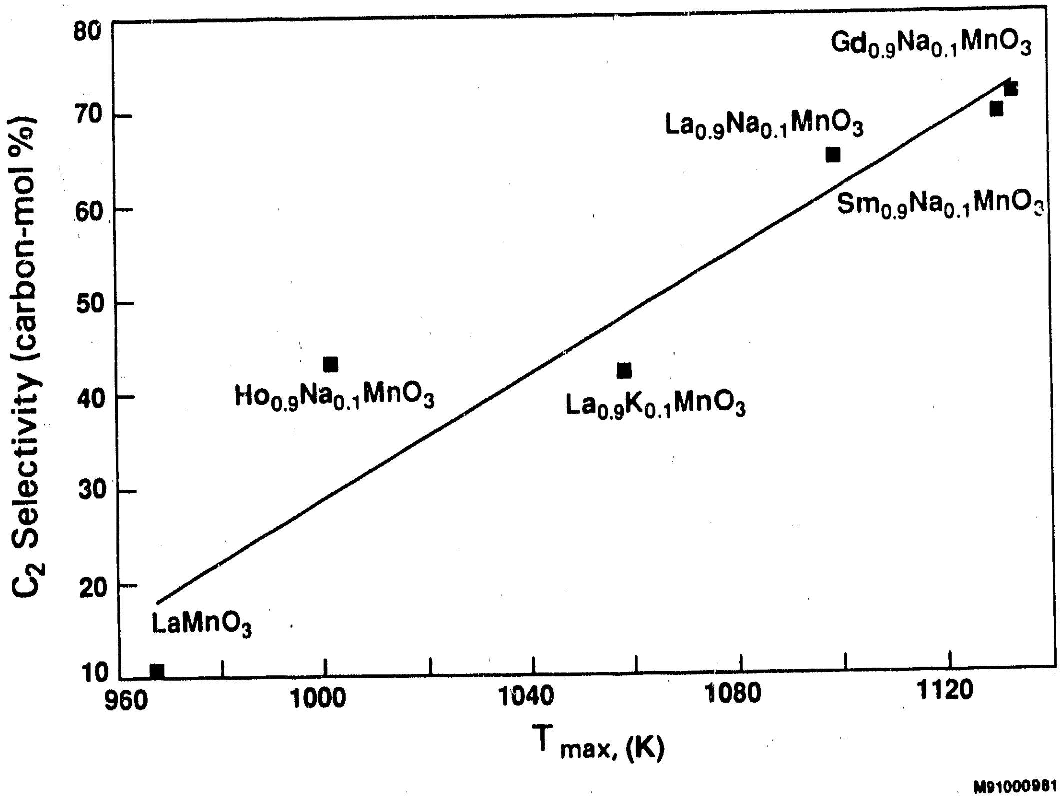

Figure 2. Correlation of C_2 Selectivity With the Temperature at Which Maximum O_2 Desorbed (T_{max}) From Perovskite Type Catalysts (0.25 g catalyst tested at 1,093 K; CH_4/O_2 ratio = 5)

reaction, which indicates that any further loss of Na is somewhat retarded. No significant change in the amount of phosphorus was observed. There was a considerable loss of sodium on the surface of the Na_2CO_3/CaO catalyst after 20 hours of reaction, with certain regions having zero sodium concentration. Atomic absorption (AA) analysis, which measures the sum of the surface and bulk sodium, of the used catalysts indicated that the amount present in each material was nearly identical. Thus, one can conclude that the stable reactivity over the $Na_4P_2O_7/CaO$ catalyst results from the enhanced stability of Na on the surface, and this stability is most likely promoted by the presence of phosphorus. It is of interest to point out that there was no sodium loss when the $Na_4P_2O_7/CaO$ material was heated to 1,101 K in the absence of the reactants. This clearly demonstrates that temperature alone is not responsible for volatilization of the sodium.

Additional information is obtained by examining the SEM photomicrographs in Figure 3. A porous structure with a uniform interconnecting network arrangement was observed on pure CaO. Doping with $Na_4P_2O_7$ led to the formation of more rounded particles and aggregates. (A similar surface structure was observed for the Na_2CO_3 doped material.) After the high temperature reaction, the surface of the Na_2CO_3/CaO catalyst still appeared to consist of agglomerated round particles. However, on the used $Na_4P_2O_7/CaO$ catalyst, the round particles or aggregates were not observed, but a uniformly distributed structure with sharp edges was now visible on the surface. Clearly, the surface morphology was somewhat modified by

(a) CaO

(b) 0.1 $Na_4P_2O_7$/CaO

(c) 0.1 Na_2CO_3/Ca) After Reaction

(d) 0.1 $Na_4P_2O_7$/CaO After Reaction

Figure 3. Scanning Electron Photomicrographs of CaO Containing Sodium Before and After Reaction

the presence of the $Na_4P_2O_7$. Although the specific nature of this modification is not entirely evident, it is probable that it is at least partially responsible for the increased stability of this material.

Low Temperature Catalyst Development

Ongoing research is focusing on the development of catalytic materials which operate in the temperature range of 550 °C. The potential of employing SMSC systems for this purpose is currently being investigated. A schematic of an SMSC system is presented in Figure 4. A thin film of the melt is deposited on the walls of a porous support material, and is present in the form of a liquid at reaction conditions. Reaction can occur either at the surface or in the liquid phase of the melt. Generally, extremely high temperatures are required to maintain a molten salt phase; however, relatively low melting points can be achieved by employing eutectic salt mixtures. Some typical compositions and melting points are presented in Table 3.

There is some precedence for the use of molten salts as catalysts, and a good general overview of the subject can be found in a review by Kenney.[13] Furthermore, there are reports from as early as 1943 that claim that methane can be converted to formaldehyde with 70% yield using a $NaBO_2/LiBO_2$ melt.[14] The use of SMSCs is not as common; however, a recent study has reported the use of these materials for the oxidation of ethylene to acetaldehyde (Wacker Process).[15]

A series of preliminary experiments has been conducted with a variety of the eutectic melts. Unfortunately, after reaction the surface area was completely destroyed, most likely because of plugging of the pores. Efforts are now being directed towards lowering the melt loadings and identifying support materials with larger pore diameters to overcome this obstacle. Surprisingly, however, the pure support itself

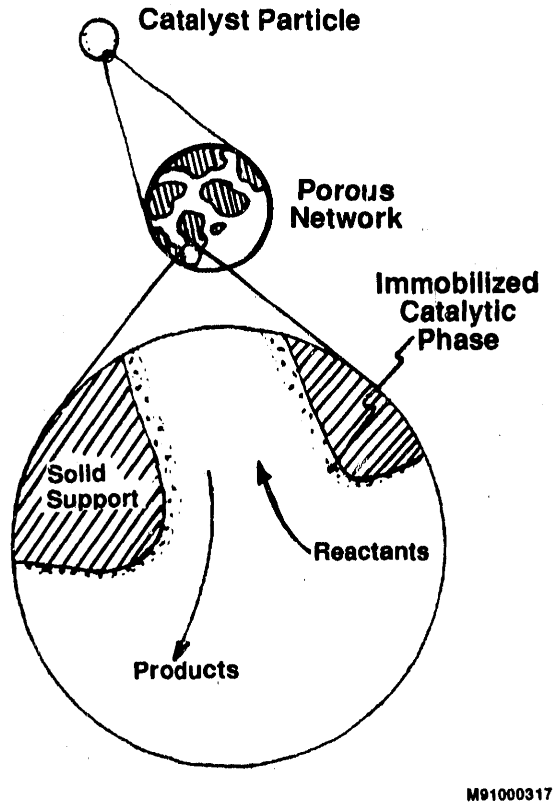

Figure 4. Schematic of the Supported Molten Salt Catalysts

Table 3. Typical Eutectic Molten Salt Compositions

A-B	Mole % B	T_{mp} (°C)
Li_2CO_3-Na_2CO_3	50	505
LiCl-KCl	42	361
LiCl-KCl	40	450
KCl-$PbCl_2$	88	428
KCl-$MgCl_2$	33	435
Li_2CO_3	--	891

has shown reasonable activity for the formation of formaldehyde, and a summary is presented in Table 4. No attempts were made to maximize the formaldehyde production; however, the yields obtained here are comparable to those obtained earlier over a variety of other active catalysts.[7] It is also important to note that these results were obtained using an oxygen rich feed

Table 4. Support Activity

Temperature (°C)	Conversion (%)	Selectivity (%)					Yield (g/kg catalyst/h)
		CO	CO_2	C_2H_6	C_2H_4	H_2CO	
500	1.5	2.5	0.9	0.0	0.0	96.6	47.2
600	2.5	15.9	3.4	0.0	0.0	80.7	65.8
700	8.2	63.7	7.5	0.9	0.0	27.9	71.0
800	26.4	79.6	9.7	3.0	1.4	6.3	50.6

P = 1 atm; Flow Rates: CH_4:O_2:He 20:10:20 mL/min; 0.5g catalyst

rather than the oxygen lean conditions that are generally employed. These results are encouraging and therefore, in addition to developing the SMSC materials, a portion of our research efforts will be directed towards studying this reaction system.

SUMMARY AND CONCLUSIONS

- A number of new material compositions have been identified that are capable of promoting the conversion of methane to ethane and ethylene with yields of 20%.

- In addition to being able to catalyze the conversion of methane, several of these materials appear to exhibit considerably higher stability than previously identified methane conversion catalysts.

- Temperature programmed desorption studies have indicated that product selectivity is directly related to surface oxygen bond strength.

- The use of sodium pyrophosphate as an alkali metal dopant increases catalyst stability. Surface analysis indicates that phosphorus stabilizes sodium on the catalyst surface, and may also modify the morphology of the surface.

FUTURE WORK

- Continue to examine the potential of employing supported molten salt materials as methane conversion catalysts.

- Continue efforts to identify and develop novel, low temperature processes for the conversion of methane.

- Continue to conduct fundamental studies in an effort to identify the overall reaction mechanism for the activation and conversion of methane. In addition to the characterization techniques previously mentioned, temperature programmed reaction (TPR) studies employing ^{13}C ethane and ethylene will be conducted in an effort to (1) determine the origin of the non-selective CO and CO_2 products and (2) identify and define technological limitations of the reactions (e.g., is C_2+ yield restricted to < 25%).

ACKNOWLEDGMENTS

Participation of the following ORAU students in this project is greatly appreciated: postdocs - M.Q. Ahsan and Khurram Zahir; undergraduates - Jennifer A. Roth and Keith A. Walter.

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Poster Session

The Geoscience Center at METC

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ABSTRACT

The focal point of research activities on gas projects at METC is the Geoscience Center, which houses the tools and data to evaluate conventional, unconventional, and speculative gas resources in the United States as sources for future gas resources. The Center's capabilities are designed to meet the present and future needs of projects as outlined in the gas plan. Specific project problems being addressed include the evaluation of horizontal drilling sites and techniques for reservoir characterization. Production performance analyses have been started and will be improved upon using an integration of geotechnical data and software to formulate models of the reservoirs. Data base activities concentrate on the standardization and transfer of present paper and magnetic media to optical and magneto-optical media for more efficient access and processing. Technology transfer is a continuing effort using present and innovative mechanisms such as optical disk, computer assisted 3-D modeling, and video displays to communicate information and results to ultimate users. This information is structured for the dual purpose of (1) providing general technical support for independents and other companies, and (2) for implementation of specific exploration and production technologies tailored to a particular region.

Eastern Gas Analysis - A Systems Approach

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ABSTRACT

Eastern Gas Systems Analysis studies are being performed at the Morgantown Energy Technology Center (METC) to determine the conditions under which gas produced through application of advanced technologies is economically attractive. For advanced technologies such as horizontal drilling in the Devonian shales, these conditions are determined through the use of geologic screening and computer simulations of gas production, reservoir stimulation , and economic-risk analysis. Conditions for attractive economics include acceptable profitability/rate of return (ROR), and increased market share for the gas. Electric utility gas consumption is expected to grow from its 1988 level of 2.63 trillion cubic feet (Tcf) to 5.92 Tcf by the year 2010. METC is developing a market share analysis methodology to identify and overcome barriers that prevent advanced technologies from increasing their gas share in the electric utility market. Competitive prices and profitability are potentially significant barriers. This methodology uses probabilistic economic analysis to quantify risk and provide more insight into the actual profitability. The current focus is on examining horizontal well economics for eastern Devonian shales and probabilistic techniques to address profitability.

In the area of advanced technology economics, METC has developed a simulation methodology that determines the probability distribution of the horizontal well costs required to achieve a given target ROR. This methodology requires probability distributions for variables such as gas price, gas production, and ROR. A risk analysis model samples these distributions and analyzes the well cost to achieve the input ROR values. This is accomplished through an internal user-developed cash-flow model that yields a probability distribution of well costs. This model is being utilized to help provide guidance in planning and designing efforts on DOE horizontal well projects.

Systems Analysis of Natural Gas Resources From Low-Permeability Formations

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ABSTRACT

The Morgantown Energy Technology Center (METC) conducts systems analyses that are focused on guiding and supporting the natural gas program goals of the U.S. Department of Energy (DOE). The purpose of the DOE Gas Research Implementation Plan is to provide a basis for greater utilization of the nation's natural gas resource by (1) enlarging and stabilizing the domestic gas supply reserve base (leading to increased public confidence in the long-term availability of affordable gas), and (2) increasing production from low-permeability formations. Use of the systems methodology is essential for reaching these goals, which include defining research activities aimed at improving extraction technologies. Industry use of these technologies is expected to expand the domestic reserve base of natural gas.

A tremendous resource potential exists for gas-bearing low-permeability formations, and part of DOE's gas research program targets this resource. In general, the issue of natural gas from low-permeability formations is not whether natural gas is present or where the gas exists, but rather, <u>economical</u> production of the resource.

Activities in the Western Gas Systems Analysis project include four specific tasks:

- Target high-potential resources.
- Estimate reserves as a function of technology and price.
- Assess improved and alternative extraction technologies.
- Define and prioritize extraction research.

To accomplish these tasks, the methodology includes four types of modeling:

- Geologic Modeling, yielding new and enhanced geologic characterizations.
- Technology Performance Modeling, or providing estimates of the recoverable gas as a function of extraction technology.
- Cost Engineering Modeling, analyzing investments as a function of region and geology.
- Financial Modeling, coupling technology with economics leading to estimates of natural gas reserves.

METC's systems efforts quantify reserve additions based on alternative extraction technologies. Technologies being evaluated include improved fracturing and horizontal well completions. Improved stimulation includes longer induced fractures, the use of fluids less damaging to the formation, and increased fracture conductivity. In addition, the impact of infill drilling, which could access by-passed reservoirs, is being assessed.

Current systems analyses have focused on the Washakie and San Juan Basins, located in Wyoming and New Mexico, respectively. The Washakie Basin is a subbasin of the Greater

Green River Basin (GGRB). (See Figure 1.) The GGRB is of great interest because of

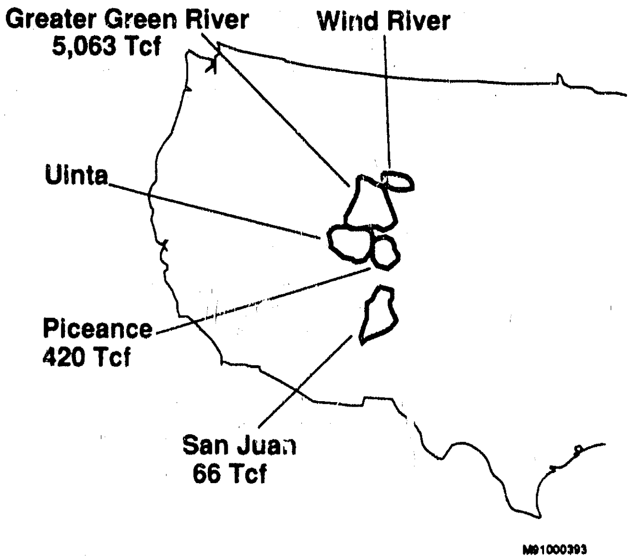

Figure 1. Gas Resource Estimates From Low-Permeability Formations, Rocky Mountain Region

its considerable potential; a recent estimate of the in-place gas resource for the GGRB is 5,000 trillion standard cubic feet (Tcf).[1] The same estimate shows 1,070 Tcf in the Washakie Basin. (See Figure 2.) Presently, an enhanced geologic model of the gas-bearing formations underlying the Washakie Basin is being finalized. Preliminary review of the data indicates an in-place resource on the order of 500 Tcf for the subbasin. A comparison of the final resource estimate and the in-place volume derived from the United States Geologic Survey's study of the GGRB will be completed.

Analysis of the low-permeability formations underlying the San Juan Basin has been completed. Results of that systems study indicate that technically recoverable gas remaining in the low-permeability areas of the San Juan Basin amounts to 6.8 Tcf. Additions to "booked" reserves total 2.1 Tcf (at $2.00/ thousand standard cubic feet [Mcf]) from the San Juan's low-permeability sandstones, while the use of improved well stimulation methods can provide another 1.7 Tcf of economically recoverable gas. More than 80% of the incremental gas (1.4 Tcf of the 1.7 Tcf) available through more efficient hydraulic fracturing is present in the Dakota Formation.

REFERENCE

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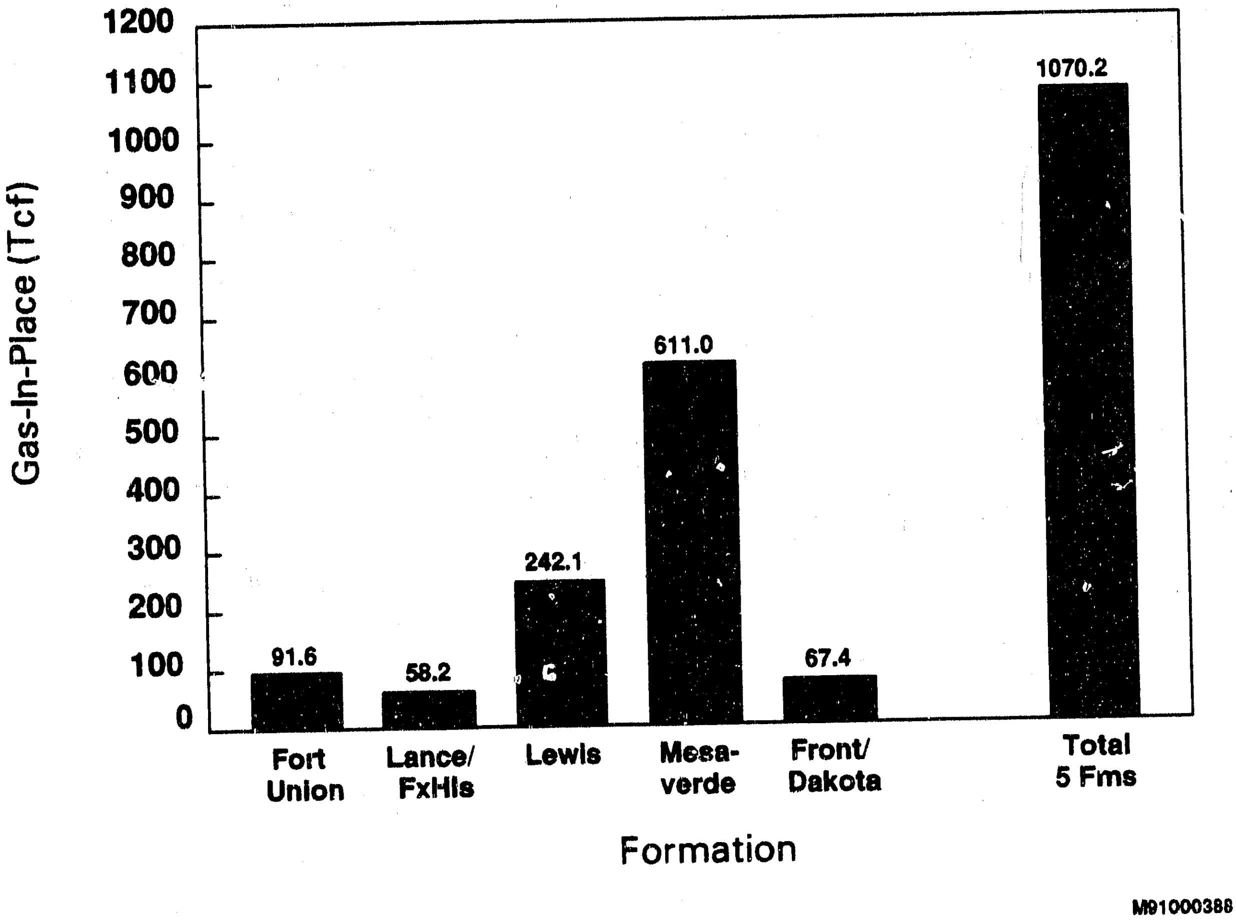

Figure 2. Washakie Basin Gas-In-Place Estimates
(U.S.G.S. 1988)

Geotechnical Evaluations for Siting Horizontal Wells in Devonian Shale Reservoirs

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ABSTRACT

Several geologic mapping techniques, including geophysical and geochemical surveys, are used to define the orientation and production potential of fractured fairways in the Devonian shales. A flow sheet was developed for the evaluation of each site to determine if reservoir criteria are met to drill the well. The input data vary for each area and is dependent on data availability.

Two, directional, well site evaluations are presented to show well-siting rationale and, ultimately, well-design geometry. Detailed analyses of well-log data and surface geology were used to develop a three-dimensional model of the reservoir target. Seismic data were integrated, where available, to enhance detection of increased fractured porosity. The relationship of near-surface fracture trends to subsurface geologic structure was delineated using soil gas and water geochemistry and dual depth resistivity surveys. The data were integrated to form a reservoir model of the potential site and a form basis for well design.

The two sites include a high-angle well project in Roane County, West Virginia, and a horizontal well project in Putnam County, West Virginia. The Roane County site utilized well data, geology, and soil gas chemistry to define fracture fairways, site the well, and formulate the well design. The Putnam County site was evaluated using similar data, plus water geochemistry, remote sensing, and shallow resistivity surveys.

The methodology has proven successful in delineating enhanced fracturing related to gas production from the Middle Devonian shale sequence in the Appalachian Basin.

Western Tight Gas Sands Research

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ABSTRACT

This poster session displays several of the projects completed during the past year as part of the METC in-house research on the Western Gas Sands Project.

The first project's objective was to evaluate the effectiveness of the computerized technique of coplanar lineament analysis in the exploitation of natural gas from tight sandstones. It was thought that the lineaments could be an aid in locating subsurface fractures, which would enhance the production of gas from sandstones with low matrix permeability.

The study was conducted with satellite-acquired topographic data on a portion of the Douglas Creek Arch in northwestern Colorado. This area has significant gas production from the Upper Cretaceous Mancos "B" tight sandstone at a fairly shallow depth of 2,500 to 3,000 feet. The lineaments detected by the coplanar technique did not correspond with the locations of linear trends on contoured production maps nor with the locations of faults mapped at the surface. Additionally, the dominant trend of the lineaments was north-south, while northeasterly and northwesterly trends were dominant on contour maps of gas production and from analyses of joints and faults measured at outcrops and from airphotos. It is concluded that, on the Douglas Creek Arch, coplanar lineament analysis is not effective in mapping the surface geology nor in detecting subsurface fractures.

The second project originated from work done for the coplanar lineament analysis. Since vertical wells to the Mancos "B" are uneconomical over much of the Douglas Creek Arch, a horizontal wellbore is suggested as a possible means of economically developing the natural gas in the Mancos "B" sandstone. Subsurface mapping, using electric well logs, of the interval thickness between the top of the Upper Cretaceous Morapos Formation and the top of the Upper Cretaceous Mancos "B" Formation reservoir sandstone suggested the presence of several, northeasterly trending, normal faults in many of the wellbores on the Douglas Creek Arch. It was also noted that, away from the area where the Mancos "B" has good porosity and good gas production, linear trends of better gas production corresponded with some of these subsurface faults. Both the subsurface faults and the linear production trends corresponded closely with normal faults mapped at the earth's surface. The correspondence of faulting and better gas production makes it reasonable to conclude that the Mancos "B" is more highly fractured near the faults. The best location to attempt a horizontal well is near one of the subsurface faults with the well oriented in a direction perpendicular to the fault and its associated fractures.

The third project points out that horizontal well technology can also be applied to develop tight blanket gas sandstones in the Greater Green River Basin. The Greater Green River Basin was chosen for study because of its enormous gas resource (5.1 trillion cubic feet [Tcf]) estimated by the USGS. The particular area on the northeast flank of the Washakie sub-basin was selected because of the presence of a tight, currently non-commercial, blanket, gas-producing sandstone at an approximate depth of 10,000 feet, which is about the current depth limit to which horizontal wells can be economically completed.

The objective of the fourth project, which was done by the on-site contractor, was to determine the amount of gas produced from tight gas sands in the states of Wyoming, Utah, Colorado, New Mexico, and Montana. The study determined that, through December 1988, 804 billion cubic feet (Bcf) were produced from 2,903 tight gas wells, and the annual production for 1988 was 96 Bcf. To obtain these figures, a tape was furnished to METC by The Federal Energy Regulatory Commission (FERC) containing all the wells designated by FERC to be eligible for incentive pricing as a result of the Natural Gas Policy Act of 1978. Using the API (American Petroleum Institute) well identification number of tight wells from the FERC tape, the gas production was obtained for those wells from tapes of annual gas production purchased from Dwight's, Inc.

Deep Source Gas
Seismic Survey - Washington State

Mary Guide
Steven C. Krehbiel
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ABSTRACT

Deep Source Gas Research is intended to investigate the hydrocarbon potential of deep sedimentary basins in unexplored and unconventional areas. In particular, the relationship between plate tectonics, sedimentary deposition, and hydrocarbon generation is a subject of special interest. A regional geophysical study of southwest Washington, using a method known as magnetotellurics, found anomalous rock characteristics in an area roughly bounded by Mt. Rainier, Mt. St. Helens, and Mt. Adams. This anomaly could be caused by the presence of a large volume of organically enriched sediments which, if present, could act as source rocks for natural gas generation. A seismic reflection survey was sponsored by METC to further investigate this possibility. Four METC seismic lines totalling 147 km and one 53 km commercial seismic line were obtained from 1988 to 1989.

Currently, work on this data is nearing completion. Preliminary interpretation appears to support the possibility of a large volume of deeply buried sediment as indicated by the magnetotelluric data. The seismic reflection data depicts a complex geologic history of the area involving deposition of early to mid-Eocene sediment followed by emplacement of intrusives and the development of the current volcanic environment. It is well documented that the most recent geology of the area is dominated by the presence of an active subduction zone, where the ocean floor is being overridden by the continental margin. The early Eocene sedimentary environment appears to have been effected by a similar subduction process which occurred to the east of the currently active zone. The stratified nature of the reflectors within the magnetotelluric anomaly area could indicate low energy sedimentary deposition. Sediment of this type may have been deposited in a forearc basin or as trench fill, both of which could be favorable to natural gas generation.

Future work will include the integration of new seismic reflection data acquired this summer along with a METC-sponsored study of the local surface geology. The final interpretation will be used to propose a drill site for stratigraphic and hydrocarbon potential evaluation.

Parametric Studies on Catalytic and Non-Catalytic Partial Oxidation of Methane, Ethane, and Ethylene

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Morgantown Energy Technology Center

SUMMARY

The objectives of this project are (1) to perform short- and long-term studies to identify new concepts for, and the technological barriers to, developing a process to convert natural gas to liquid fuels; (2) to identify critical parameters such as contact time, temperature, pressure, and oxygen to methane ratio; and (3) to provide technological support to project managers, private industry, and the scientific community.

Catalytic and non-catalytic partial oxidation of methane, ethane, and ethylene have been investigated at several reaction conditions. Significant gas-phase reactions were observed at higher pressure, oxygen to methane ratio, and contact time. It appears that activation of methane occurred both in the gas phase and on the surface of perovskite-type catalysts; the surface reactions are important in oxidizing CH_3, C_2H_6, C_2H_4, and CO to carbon dioxide. The results also indicate that simultaneous operation at high pressure and temperature is a major problem, and at these conditions, a significant amount of higher hydrocarbons are being converted to carbon oxides.

Ethylene is the preferred product of methane conversion, and it is formed mainly from the dehydrogenation of ethane in the gas phase. Experiments were performed to identify the effects of pressure, temperature, and contact time on partial oxidation of ethane and ethylene in order to understand the reaction mechanisms, which may aid us to identify a better process with a better activity and selectivity to higher hydrocarbons. During partial oxidation of ethylene in the absence of methane, a significant amount of carbon deposited on the reactor walls; the major products were oxygenated-ethylene products (C_2H_4O). Furthermore, ethylene was the major product of oxidative dehydrogenation of ethane, with less than 5% conversion at atmospheric pressure and 550 °C.

BACKGROUND

The oxidative coupling of methane to a storable liquid fuel is a desirable alternative to compressed natural gas. Abundant reserves of natural gas exist in locations too remote from market areas to be recovered on a commercial basis by present methods.

We have shown that by proper cation substitution in perovskite-type oxides, active and selective catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained.[1-3] Recent studies showed that phase-phase reactions, especially at higher pressures, play a significant role in the partial oxidation of methane.[4-6] Therefore, in order to gain further insight into these catalytic and non-catalytic systems, the effects of temperature and pressure on catalytic and non-catalytic conversion of methane to C_2+ hydrocarbons were investigated at several reaction conditions, both in the presence and in the absence of perovskite-type oxide, $La_{0.9}Na_{0.1}MnO_3$.

The results of catalytic studies at METC have shown that by proper cation substitution in perovskite-type oxides and by supporting sodium pyrophosphate on metal oxides ($Na_4P_2O_7/Gd_2O_3$ and $Na_4P_2O_7$/CaO), superior catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained. The catalysts developed at METC were found to be active, selective, and stable for the oxidative coupling of methane. Surface analysis indicated that phosphorus stabilizes the sodium on the surface, which in turn enhances the longevity of these catalysts.[7-8] The C_2 yields for these catalysts at the maximum conditions ranged from 20 to 23% (these values are still too low for good economics).

EXPERIMENTAL SECTION

The catalyst preparation and experimental procedures have been reported elsewhere.[1] A 0.235-m long alumina reactor tube (9.53 mm outside diameter [o.d.], 6.35 mm inside diameter [i.d.], calculated heated volume 2.0 cm^3) with a quartz thermowell was used as a fixed-bed reactor to evaluate the catalysts (0.5 g and -28/+48 mesh). Electronic mass flow controllers were used to feed methane (99.99%), oxygen (99.8%), and helium (99.999%). The reactor was electrically heated to reaction temperatures under a flow of helium. Product analyses were performed by on-line gas chromatography (GC) and mass spectrometry (MS). Products were analyzed for carbon monoxide, methane, ethane, ethylene, propene, propane, hydrogen, carbon oxides, formaldehyde, and water. A thermal conductivity detector was used with a 1 m x 3.2 mm o.d. stainless steel molecular sieve 5A column and a 3.7 m x 3.2 mm o.d. stainless steel Porapak Q (80/100 mesh) column. Results are reported on a carbon-mol % basis.

RESULTS

The dependence of conversion and selectivity on temperature for oxidative coupling of methane in an empty alumina reactor is shown in Figure 1, at 101.3 kP pressure and a methane to oxygen ratio of 2:1. At low temperature, ethane and formaldehyde (not shown in the graph) appeared to be the major products, and their concentrations decreased with increasing temperature. The amounts of CO and CO_2 were also increased, with carbon monoxide being the predominant product. Furthermore, higher methane and oxygen conversions were observed at higher temperatures. However, with increasing temperature, the selectivity to ethylene reached a maximum and then declined, indicating that ethylene was converted to carbon oxide, mainly carbon monoxide, at higher temperatures.

The importance of the gas-phase contribution can be seen in Figures 2 and 3. Figure 2 shows the results obtained in the reactor with dead volume (contact time = 2.4 s), and Figure 3 shows the results obtained when the dead volume was minimized (contact time = 0.4 s). In the reactor with dead volume, as the temperature increased the methane conversion, the amounts of ethylene and CO_2 increased. However, the amount of ethane decreased while the amount of CO reached a maximum. Furthermore, when the dead volume was reduced (Figure 3), the results show an increase in the amounts of ethylene and CO with increasing temperature, but the amount of CO_2 decreased. Experiments in the reactor with minimized dead volume, in the presence and absence of the catalyst, showed that $La_{0.9}Na_{0.1}MnO_3$ contributed significantly to the oxidative coupling reactions, and that a large portion of carbon monoxide was

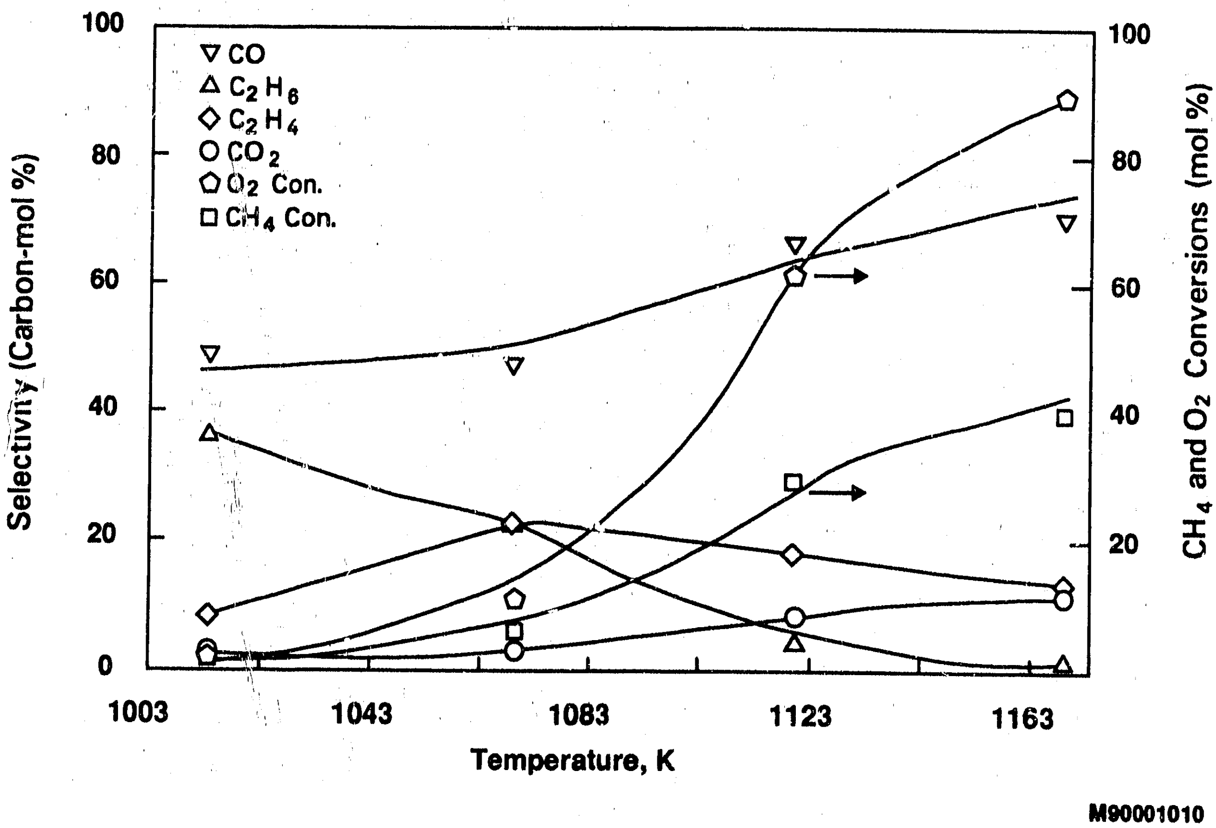

Figure 1. **Dependence of Conversion and Selectivity on Temperature in an Empty Alumina Reactor** (101.3 kP, $CH_4/He/O_2$ = 20/20/10 cm³/min NTP Flow Rates, Contact Time = 2.4 s)

converted to carbon dioxide. Higher methane and oxygen conversions were observed when dead volume was not minimized (contact time of 2.4 s), indicating that methane activation occurs both in the gas phase and on the surfaces of the catalyst.

The effect of pressure on the oxidative-coupling reaction of methane in an empty reactor is shown in Figure 4. Conversion of methane and oxygen increased with increasing pressure. The major products at 101.3 kP are ethane and formaldehyde, and their concentrations decreased in favor of carbon oxides, mainly carbon monoxide, with increasing pressure. The concentration of ethylene reached a maximum at approximately 170 kP.

The pressure dependence of conversion and selectivity over the $La_{0.9}Na_{0.1}MnO_3$ catalyst at 873 K is shown in Figure 5. A trend similar to that in the empty reactor was observed for methane and oxygen conversion. The major product in the presence of the catalyst was carbon dioxide, and its concentration decreased in favor of carbon monoxide with increasing pressure. Since carbon monoxide is the product of gas-phase reactions, this shows the significance of

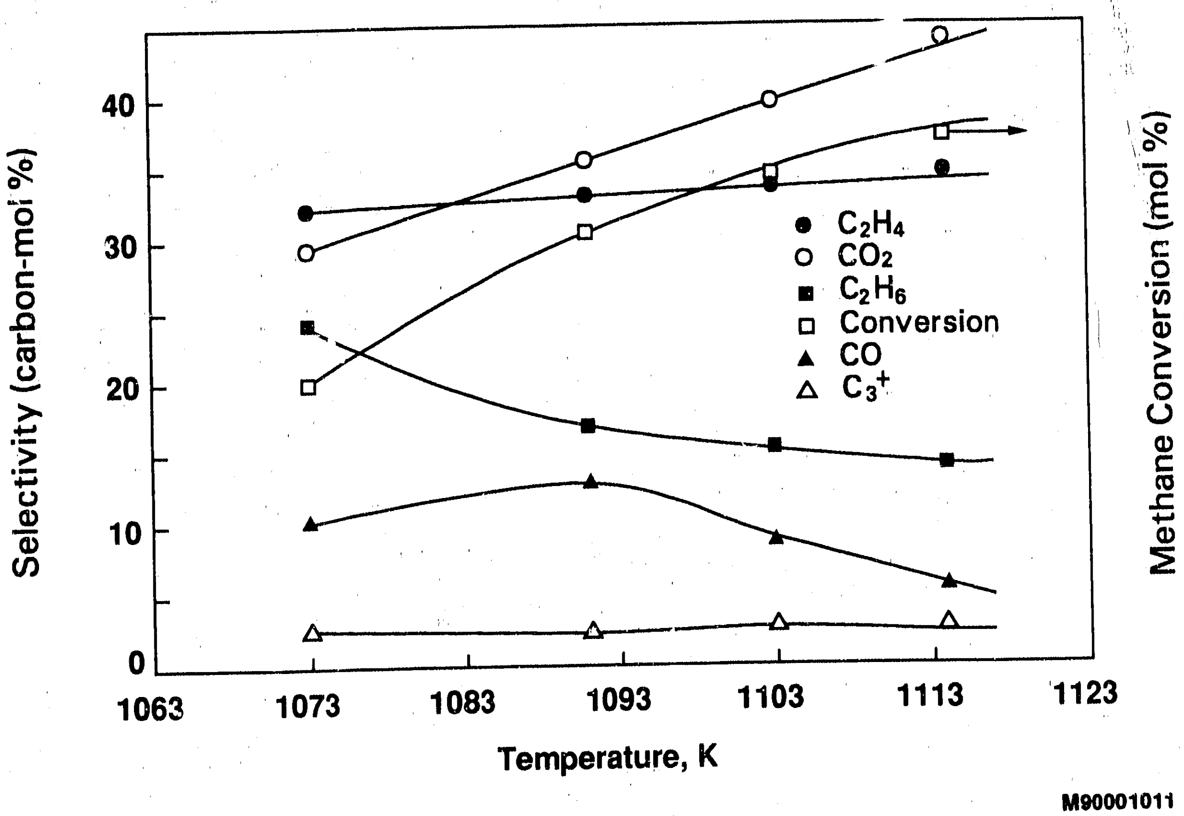

Figure 2. Dependence of Conversion and Selectivity on Temperature Over 0.50-g $La_{0.9}Na_{0.1}MnO_3$ (101.3 kP, $CH_4/He/O_2$ = 20/20/10 cm³/min NTP Flow Rates, Contact Time = 2.4 s)

the gas-phase contribution at higher pressures. The expanded portion of the graph (left axis) shows that the concentration of both ethane and ethylene reached a maximum and then declined at higher pressures, indicating that at higher pressure, the intermediates, ethane and ethylene, are being converted to carbon monoxide. As the temperature increased from 873 to 1,033 K, the gas-phase contribution also increased as shown in Figure 6. The major products at 101.3 kP are carbon dioxide, ethane, and ethylene. The concentrations of ethane and ethylene decreased as the amount of carbon oxides increased with increasing pressure. Pressure appeared to increase the contact time of the reactant.

An experiment on the effect of contact time on conversion and selectivity was performed to understand this phenomenon. The dimensionless contact time was increased from 0 to 1.0 and the results are presented in Figure 7. A sharp increase was observed for both methane and oxygen conversions by increasing the contact time. The major products at the lower contact time were ethane, formaldehyde, carbon monoxide, and ethylene. However, the major product at a higher contact time was carbon monoxide.

Ethylene is the preferred product of methane conversion, and it is formed mainly from the

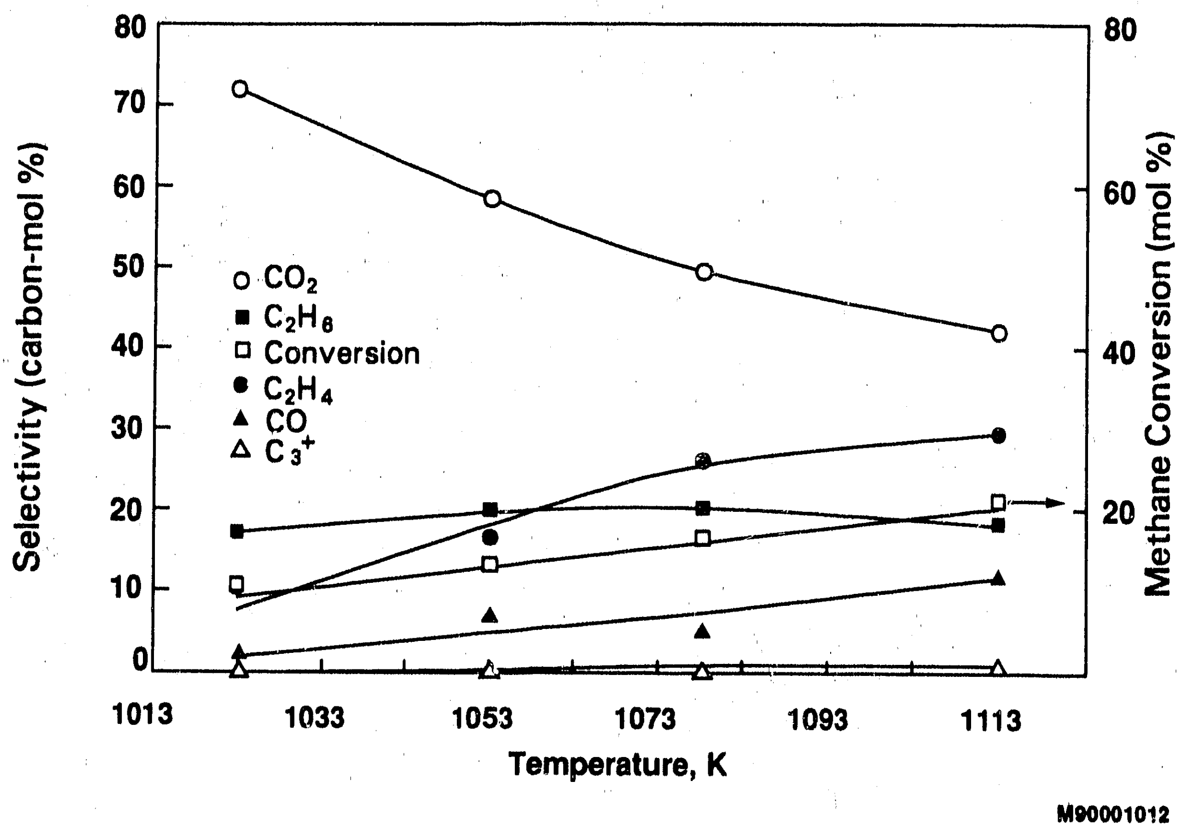

Figure 3. Dependence of Conversion and Selectivity on Temperature Over 0.50-g $La_{0.9}Na_{0.1}MnO_3$ (101.3 kP, $CH_4/He/O_2$ = 20/20/10 cm^3/min NTP Flow Rates, Contact Time = 0.4 s)

dehydrogenation of ethane in the gas phase. Experiments were performed to identify the effect of pressure, temperature, and contact time on partial oxidation of ethane and ethylene in order to understand the reaction mechanism; this may aid us to identify a better process with a better activity and selectivity to higher hydrocarbons. During partial oxidation of ethylene, in the absence of methane, a significant amount of carbon deposited on the reactor walls, and the major products were oxygenated-ethylene products (C_2H_4O). Furthermore, ethylene was the major product of oxidative dehydrogenation of ethane, with less than 5% conversion, at atmospheric pressure and at 550 °C.

CONCLUSION

We have shown that the activation of methane, ethane, and ethylene occurred both in the gas phase and on the surfaces of a catalyst. In the gas phase, diatomic oxygen may have played an important role in activating these species. Gas-phase reactions can be minimized by reducing the dead volume of the reactor. It appeared that carbon monoxide formed in the gas phase and was converted to CO_2 in the presence of the catalyst. This implies that surface reactions are important in oxidizing the intermediates CH_3, C_2H_4, C_2H_6, and CO to carbon

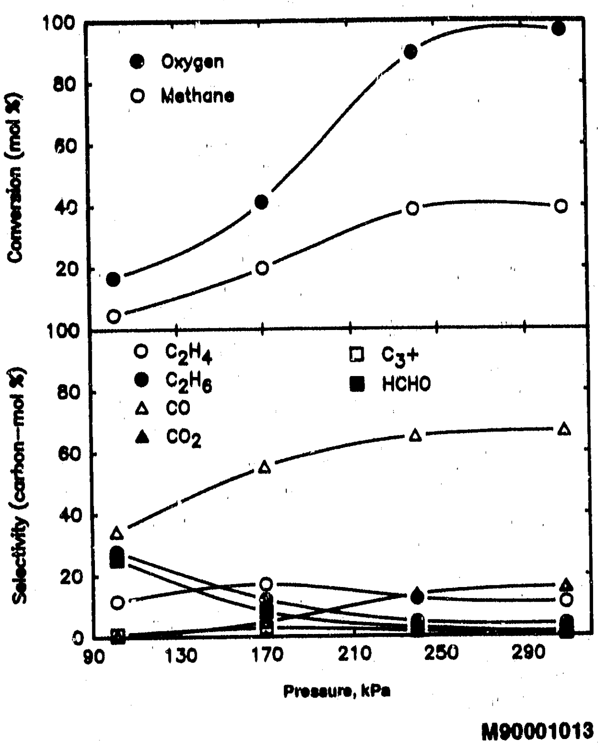

Figure 4. **Dependence of Conversion and Selectivity on Pressure in an Empty Alumina Reactor** ($CH_4/He/O_2$ = 20/20/10 cm^3/min NTP Flow Rates, 1,013 K)

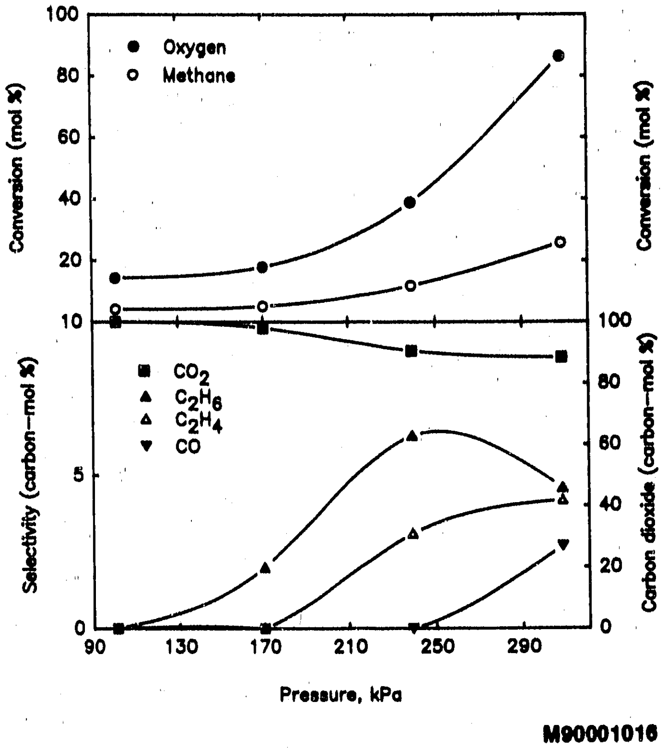

Figure 5. Dependence of Conversion and Selectivity on Pressure Over 0.50-g $La_{0.9}Na_{0.1}MnO_3$ ($CH_4/He/O_2$ = 20/20/10 cm^3/min NTP Flow Rates, 873 K)

dioxide. It was found that contact time, temperature, pressure, and the methane-to-oxygen ratio have a similar effect on the oxidative coupling of methane to C_2+ products, and are the major factors affecting the conversion and selectivity in the presence and absence of a catalyst.

ACCOMPLISHMENTS

- A peer-reviewed paper, "Oxidative Coupling of Methane Over Perovskite-Type Oxides and Correlation of T_{max} for Oxygen Desorption with C_2 Selectivity," by Abolghasem Shamsi and Khurram Zahir, was published in *Energy & Fuels*, November/December 1989, p. 727-730.

- Abolghasem Shamsi presented the paper "Effect of Temperature and Pressure on Catalytic and Non-Catalytic Conversion of Methane to C2+ Hydrocarbons" at the AIChE Spring Meeting in Orlando, Florida, March 18-22, 1990.

- Abolghasem Shamsi presented the invited paper "Catalytic and Non-Catalytic Oxidative Coupling of Methane to C2+ Hydrocarbons" at the Annual Spring Symposium of the Tri-State Catalyst Club, Lexington, Kentucky, April 18, 1990.

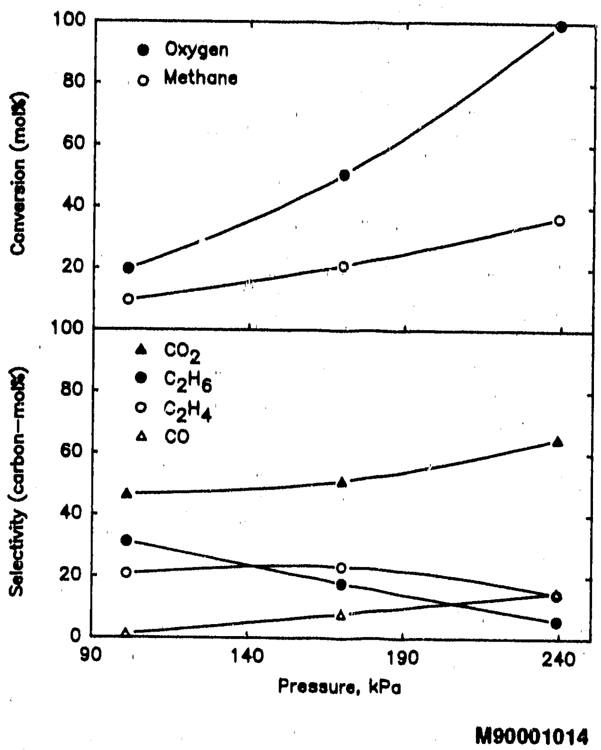

Figure 6. Dependence of Conversion and Selectivity on Pressure Over 0.50-g $La_{0.9}Na_{0.1}MnO_3$ ($CH_4/He/O_2$ = 20/20/10 cm^3/min NTP Flow Rates, 1,033 K)

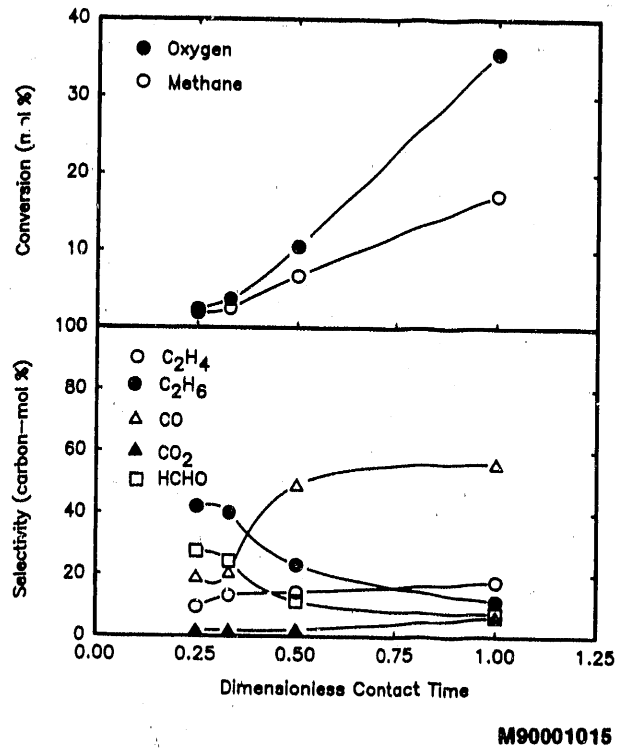

Figure 7. Dependence of Conversion and Selectivity on Contact Time in an Empty Alumina Reactor (101.3 kP, 1,013 K)

- A peer-reviewed paper, "Oxidative Coupling of Methane Over Calcium Manganate and Gadolinium Manganate Perovskites Promoted With Sodium Pyrophosphate," by Ranjani V. Siriwardane and Abolghasem Shamsi, was published in *Applied Catalysis*, vol. 60, 1990, p. 119-136.

- A peer-reviewed paper "Oxidative Coupling of Methane Over Calcium Oxide and Gadolinium Oxide Promoted With Sodium Pyrophosphate," by Ranjani V. Siriwardane, was published in *Journal of Catalysis*, vol. 123, 1990, p. 496-512.

- The paper "X-Ray Photoelectron Spectroscopic Investigation of Oxidative Coupling of Methane Over Samarium Oxide Promoted With Sodium Pyrophosphate," by Ranjani V. Siriwardane, has been accepted for publication in *Langmuir*.

- This project has provided an opportunity for one post-master and two undergraduate students to obtain valuable experience.

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Natural Gas Recovery/Utilization SBIR Program

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The U.S. Department of Energy (DOE) annually invites small business firms to submit proposals for the Small Business Innovation Research (SBIR) program. The DOE SBIR program is designed to stimulate technological innovation in the private sector, strengthen the role of small business in meeting Federal research and R&D needs, increase the commercial application of DOE-supported research results, and improve the return on investment from Federally funded research for economic and social benefits to the Nation.

The SBIR program is phased:

- Phase I concentrates on research that will contribute to proving the scientific or technical feasibility of an approach or concept (for 6½ months and up to $50,000).

- Phase II awards are to firms with approaches that appear sufficiently promising as a result of the Phase I effort (for up to 24 months and up to $500,000).

- Phase III is where small businesses pursue commercial applications of the research without Federal capital.

In the 1990 DOE SBIR solicitation, the natural gas topic was "Advanced Technology for the Recovery and Utilization of Natural Gas." The subtopics were (1) Advanced Geoscience and Geotechnology for Application to Low-Permeability Formations, (2) Advanced Geoscience and Geotechnology for Recovery of Additional Gas From Existing Reservoirs, (3) Advanced Instrumentation and Interpretation Techniques for Locating and Characterizing Natural Gas Reservoirs, and (4) Advanced Concepts for Natural Gas Conversion, Transportation and/or Utilization.

The solicitation is usually mailed in November and the proposals are submitted to DOE near the end of January. Questions about the DOE SBIR program may be addressed to Mrs. Gerry Washington, Program Spokesperson, c/o SBIR Program Manager, U. S. Department of Energy, Washington, DC 20545, telephone (301) 353-5867.

Natural gas research projects awarded under the SBIR Program and managed by METC are discussed below by the award year.

1988-1989

Development of a High-Pressure Directional Drilling System for Gas Wells was awarded to Quest Integrated, Inc. The Phase I feasibility of developing an ultrahigh-pressure downhole motor drilling system has been completed. Under Phase II, the ultrahigh-pressure motor has been fabricated and is being assembled for laboratory and field testing during the spring of 1991. Figure 1 shows how the Flow-Dril outperforms conventional drilling methods, Figure 2 is a photograph of the Tricone bit, and Figure 3 is a schematic of the ultrahigh-pressure downhole motor drilling system.

Northwest Fuel Development, Inc. was awarded a Phase I project entitled Coalbed Methane Production Using Short/Medium Radius Horizontal Drilling. Sunburst Recovery, Inc. was also awarded a Phase I project entitled

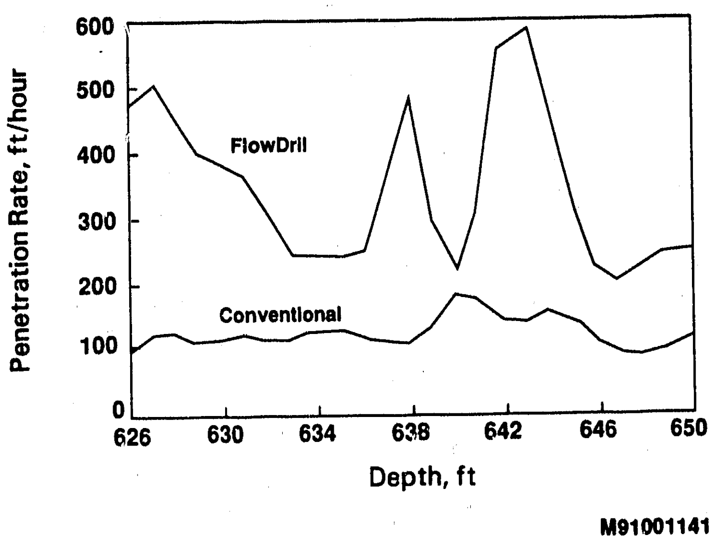


Figure 1. Field Test Results Comparison for Drilling in Colton Sandstone

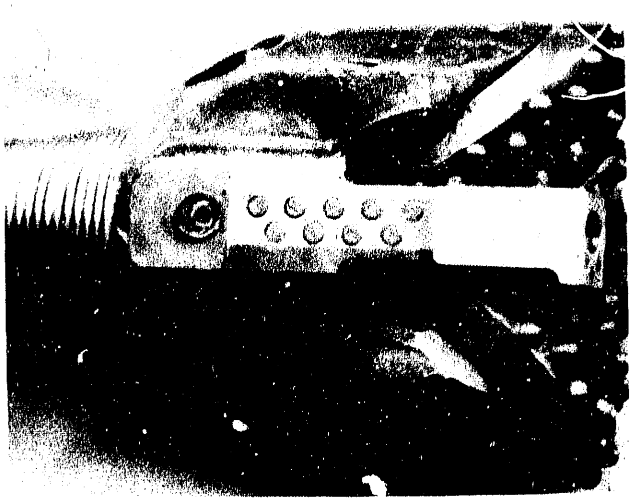


Figure 2. Tricone Bit Manifolded for Ultrahigh-Pressure Fluid Jets

Directed-Energy Fracture for Shallow Gas Strata.

1989-1990

Seven natural gas research projects were awarded in 1989-1990. Engineering Decision Consultants, Inc. was awarded a Phase I project entitled Natural Gas Self-Sufficiency Through Regional Efforts. M.L. ENERGIA, Inc. was

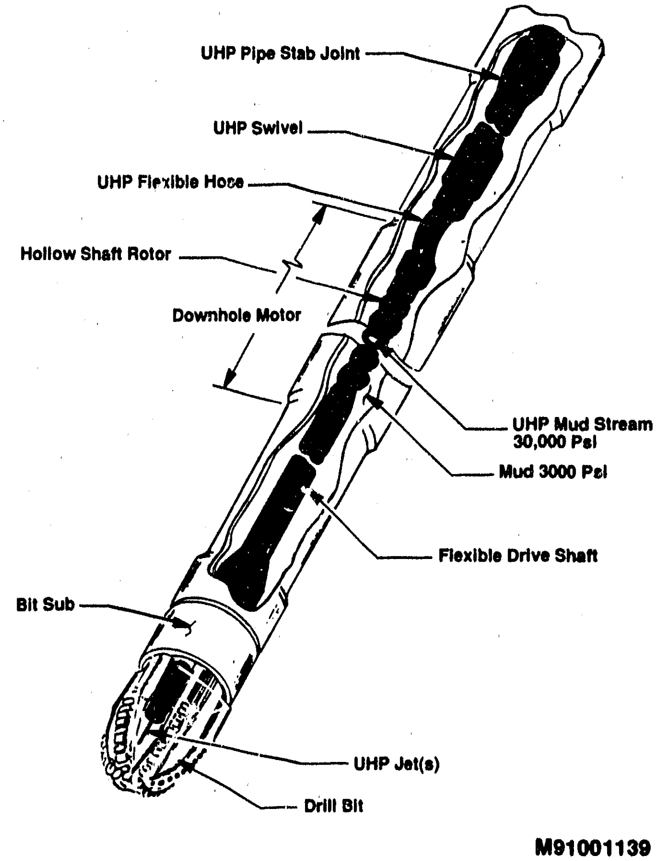


Figure 3. Ultrahigh-Pressure Downhole Motor Drilling System

also awarded a Phase I project entitled Photochemical Upgrading of Natural Gas.

Northwest Fuel Development, Inc. was awarded a Phase I and II project entitled Coal Mine Natural Gas Power Generation. The Phase I feasibility study of utilizing gob gas and abandoned mine gas to generate electric power that can be used on site at a coal mine has been demonstrated. Under Phase II, Northwest Fuel is scheduled to begin preliminary field testing of an internal combustion engine that is designed to burn the low-quality gas (as low as about 35% methane) from the coal mines in the winter of 1990-1991. Figure 4 shows the planned scheme for this testing.

Eltron Research, Inc. was awarded a Phase I and II project entitled Electrochemical Natural Gas Conversion to More Valuable

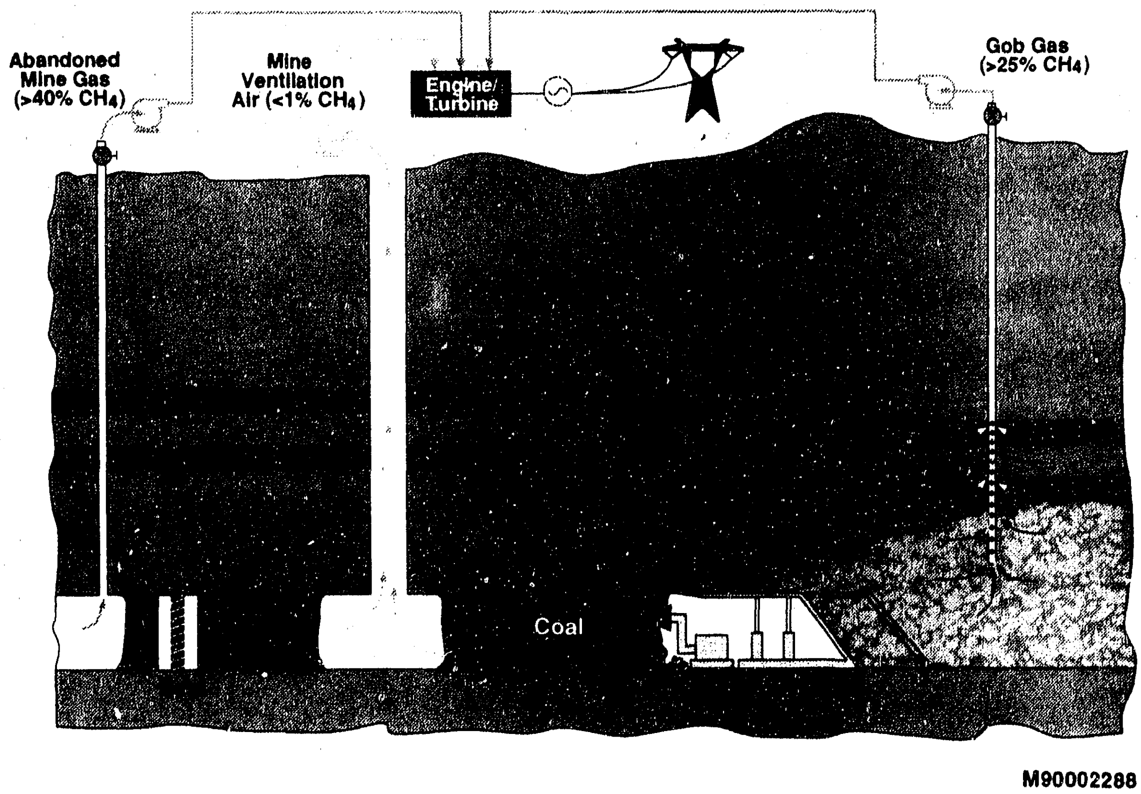


Figure 4. Schematic of Northwest Fuel's Coal-Mine Natural-Gas Power-Generation Scheme

Species. Under Phase I, the relationship has been determined between Faradaic current and the surface oxygen-binding energy of perovskite (ABO_3) anode electrocatalysts. Figure 5 is a plot of the maximum partial current density for C_2 hydrocarbon formation at perovskite anode electrocatalysts versus their calculated oxygen binding energies. Under Phase II, Eltron will demonstrate the process of perovskite anode electrocatalysts promoting the electrochemical oxidative dimerization of methane to ethylene in solid oxide fuel cells that operate at both practical rates and efficiencies. The process can be described by

$$CH_4,\ \underset{(ABO_3)}{\overset{\text{Anode}}{\text{Electrocatalyst}}}/ZrO_2(8M/oY_2O_3)/La_{0.9}Sr_{0.1}MnO_3,\ O_2(\text{Air}),$$

and is shown in Figure 6.

General Pneumatics Corporation was awarded the Phase I and II project entitled

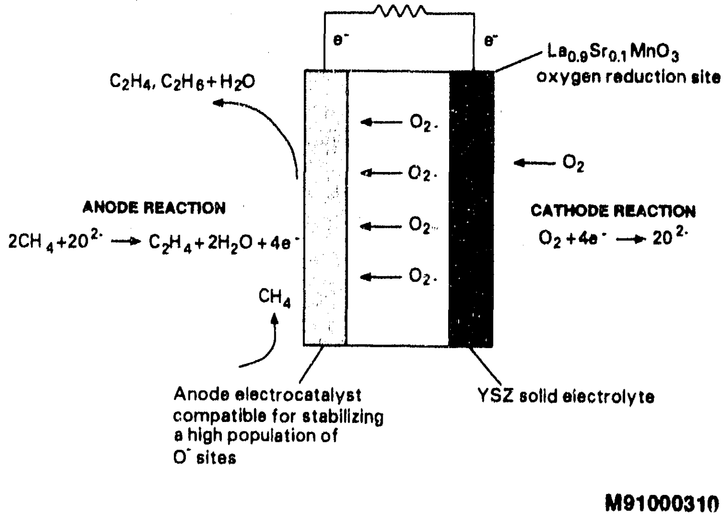
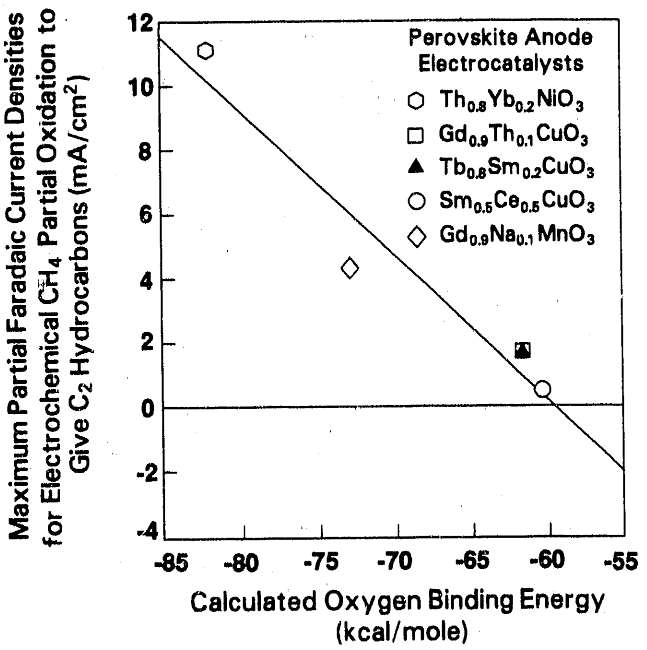
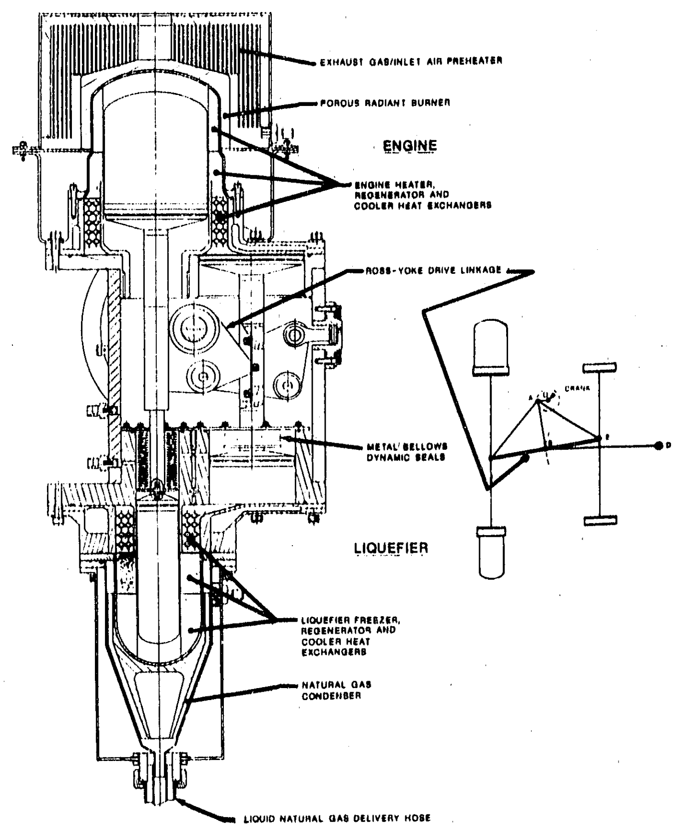


Figure 5. Demonstration of the Relationship Between Faradaic Current and the Surface Binding Energy of the Perovskite Anode Electrocatalyst



M91000380

Figure 6. Diagram of the Eltron Research Process to Convert Electrochemical Natural Gas to More Valuable Species



M91001140

Figure 7. Preliminary Design and System Features of the Gas-Fired Stirling Stirling Natural Gas Liquefier for Vehicle Fuel

Natural Gas Liquefier for Vehicle Fuel. Under Phase I, General Pneumatics has demonstrated the feasibility of their gas-fired Stirling-Stirling natural gas liquefier. The system is a Stirling Cryorefrigerator that is driven by a natural-gas-powered Stirling engine. The prototype system design is for a refrigeration capacity of 1 kW at 110 K to produce 8 liters of liquid natural gas per hour. The emphasis is on simple fail-safe operation, low-maintenance reliability, energy efficiency, and cost effectiveness for private and commercial use. The preliminary design and system features are shown in Figure 7.

Membrane Technology and Research, Inc. was awarded a Phase I and II project entitled Novel Membranes for Natural Gas Liquids Recovery. The feasibility of the process has been demonstrated. Figure 8 is a diagram of the spiral-wound module containing a composite membrane developed under the project, and Figure 9 is a process schematic that shows how the membrane system removes liquid hydrocarbons from natural gas. Figure 10 is a graph that illustrates the feasibility of the system. Membrane Technology is now working on Phase II of the project, testing of the system.

Utah Geophysical, Inc. was awarded a Phase I and II project entitled Vertical Seismic Profiling While Drilling. Under Phase I, the feasibility of obtaining a seismic profile while drilling has been demonstrated. Figure 11 shows seismic waves produced by a drill bit being recorded at the Earth's surface. Figure 12 shows unprocessed field data, and Figure 13 shows processed data where direct and reflected seismic wave arrivals are recorded. Under Phase II, Utah Geophysical is planning a well field test of the system in the summer of 1990-1991.

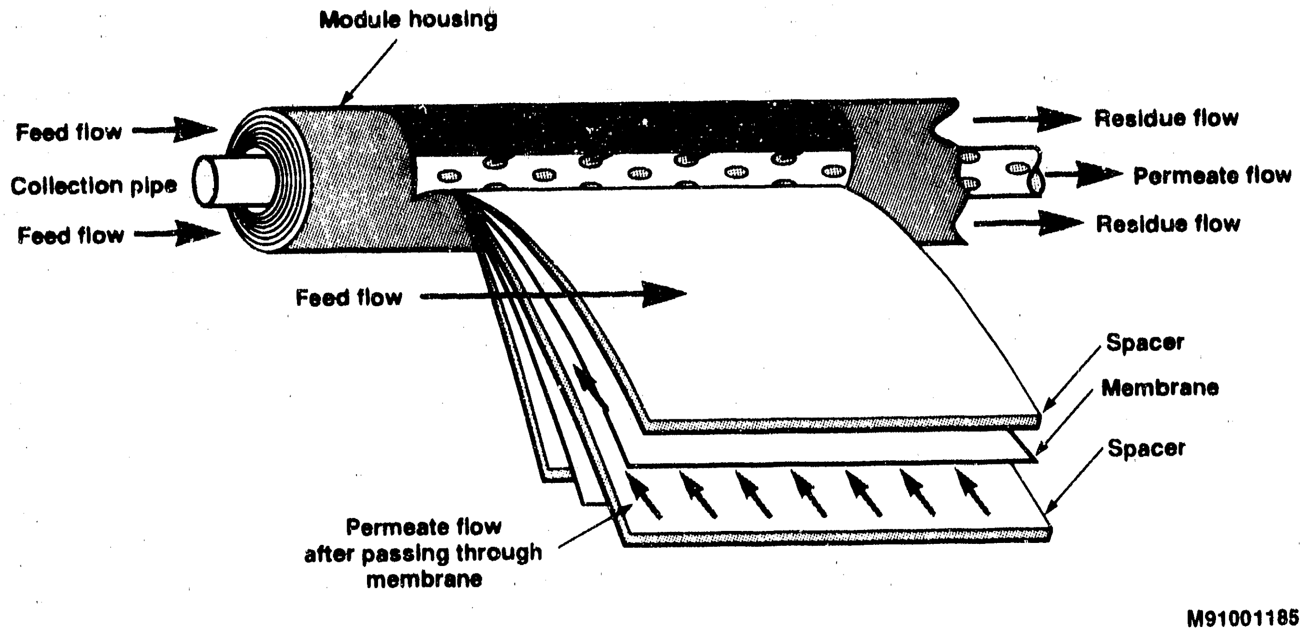


Figure 8. Spiral-Wound Module Containing a Composite Membrane

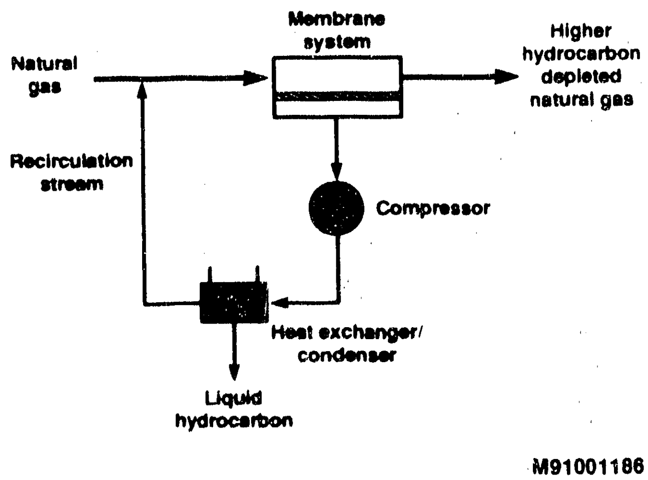


Figure 9. Schematic of Process to Remove Liquid Hydrocarbons From Natural Gas

1990-1991, New Phase I Projects

Eight new Phase I natural gas research projects have been awarded under the SBIR Program. TPL, Inc. will demonstrate the feasibility of an Ultra Fast Scintillator for Well Logging Applications. Membrane Technology and Research, Inc. will demonstrate the feasibility of Dehydration of Natural Gas by a Membrane Process.

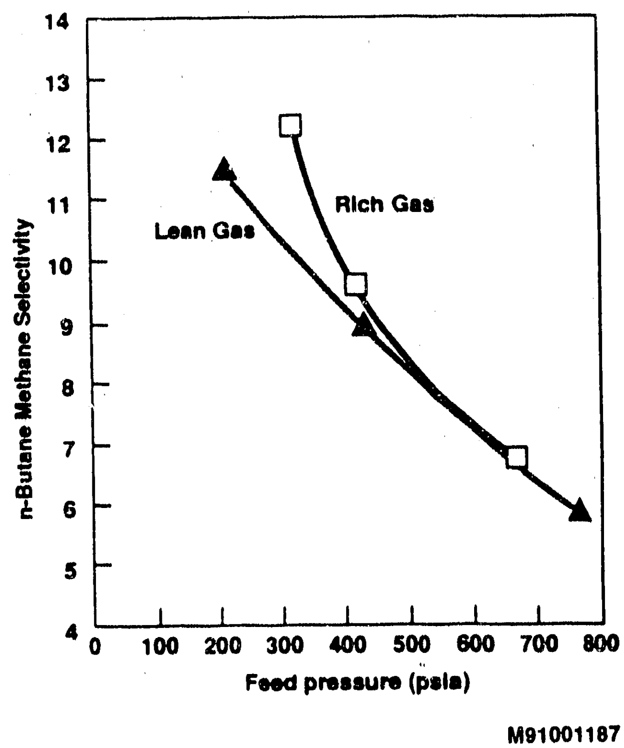


Figure 10. N-Butane/Methane Selectivity of a Selected Polyolefin Membrane as a Function of Feed Pressure for Two Hydrocarbon Gas Mixtures

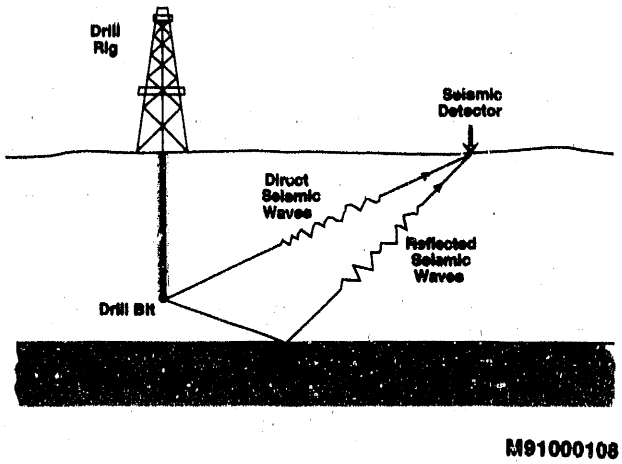


Figure 11. Schematic of Seismic Waves Produced by a Drill Bit Being Recorded at Earth's Surface

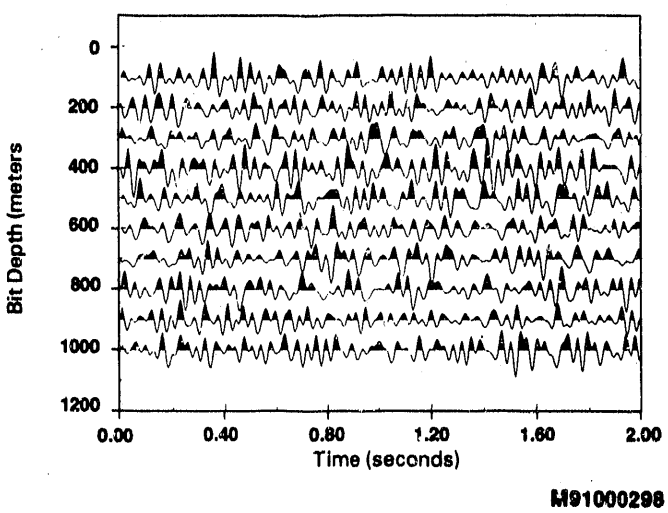


Figure 12. Unprocessed Field Data

Feasibility demonstration projects have also been awarded to Kalsi Engineering, Inc. -- Development of a Novel Sealed Bearing Assembly for Improving Downhole Motor Performance in Drilling Horizontal Wells; Northwest Fuel Development, Inc. -- Gas Turbines for Combustion of Natural Gas in Mine Ventilation Air; Star Tek, Inc. -- Reservoir-Specific Data Correlation and Transfer Methodology; and Atlantia

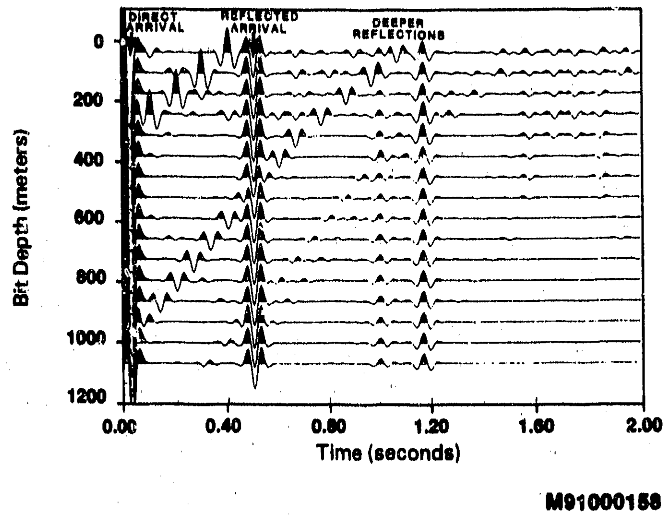


Figure 13. Processed Data Showing Direct and Reflected Seismic Wave Arrivals

Energy Corporation -- System for Economically Producing Marginal Deepwater Gas Discoveries.

StarChem, Inc. will demonstrate the feasibility of their process for Conversion of Methane to Methanol and Gasoline. In the StarChem Process, natural gas → methanol → gasoline, StarChem has taken known unit operations and put them together in a new way that reduces yield somewhat, but lowers the capital cost by a factor of three. StarChem envisions building plants in remote locations of the globe where natural gas can be acquired (produced) for as little as $0.50 per million Btu. Under these conditions, the process competes with crude oil at $20.00 per barrel. Figure 14 is a graph that illustrates preliminary results of the economics of the process.

Bend Research, Inc. will demonstrate the feasibility of a Novel Process for the Separation of Nitrogen From Natural Gas Using a Nitrogen Sorbent. Twenty-five percent, or 250 trillion standard cubic feet, of our domestic natural gas reserves are contaminated with nitrogen. If the nitrogen could be economically removed, this contaminated gas could be rendered usable. The

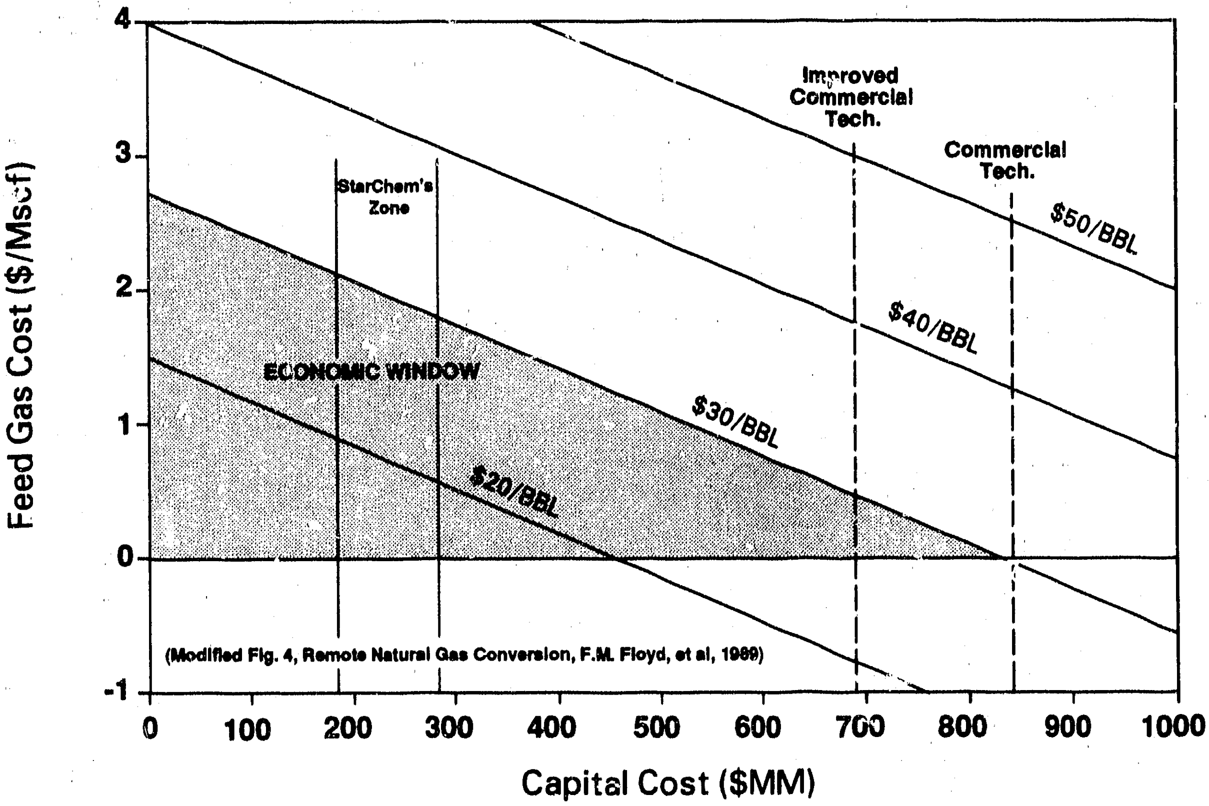


Figure 14. Gas Conversion Economics of the StarChem Process at 20,000 Barrels per Day

Bend Research process is estimated to be able to produce purified natural gas for $0.20 to $0.40 per thousand standard cubic feet. Figure 15 is a schematic of their process. Bend Research believes the Phase I feasibility of their process has been demonstrated and they have submitted their Phase II proposal for demonstrating the technology.

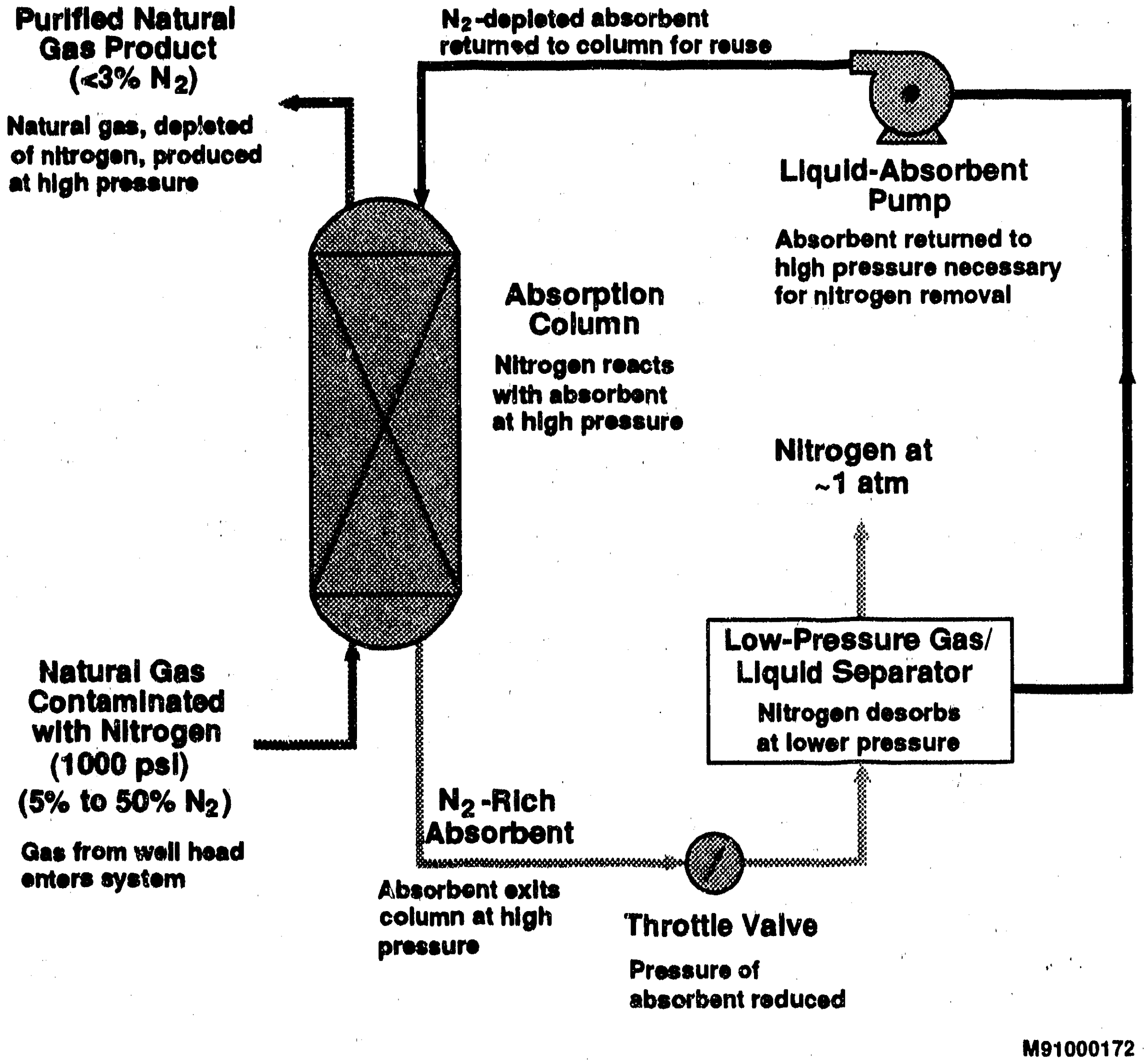


Figure 15. Schematic of the Bend Research Process to Separate Nitrogen From Natural Gas Using a Nitrogen Sorbent

The Synthesis, Characterization and Catalytic Reactions of Metal Silicate Catalysts for the Partial Oxidation of Methane

CONTRACT INFORMATION

Contract Number	FEW-6030
Contractor	Lawrence Livermore National Laboratory Livermore, CA 94550
Contractor Project Manager	Michael W. Droege, L-325 (415) 422-0155/FTS 532-0155
Principal Investigators	Michael W. Droege Lucy M. Hair
METC Project Manager	Rodney D. Malone
Period of Performance	FY 1990

ABSTRACT

We are investigating the partial oxidation and oxidative coupling of methane as catalyzed by metal silicate aerogels. The metal is placed atomically in the oxide matrix via co-hydrolysis of tetramethylorthosilicate (or ethyl) with the metal alkoxide in a suitable solvent/catalyst system. This results in a stiff gel, which is then supercritically dried to the aerogel. The resultant high surface area, on the order of 1000 m^2/g, and atomic placement of the metal make the aerogels a unique catalyst family. Metal silicate aerogels have been made with Ti, V, Y, Zr, Nb, La, Ta, W, and Sm. Reactor studies performed at 750°C, 2:1 $CH_4:O_2$, 75% Ar dilution, 50 ccm and 2 psi show that the Ti, V, Zr, Nb, Ta, and W silicate aerogels are primarily oxidation catalysts, with the Ta, W, Zr and Nb producing mostly carbon monoxide. The catalyst used was 0.3 g at a loading of about 10 wt%. Investigations at different conditions for the Zr silicate aerogel show that, contrary to thermal reactions and most catalysts, when methane conversion increases so does selectivity to C_2 hydrocarbons. This characteristic combined with its high split towards carbon monoxide prompted further investigation of the Zr silicate aerogel. First, we looked at the effect of the atomic placement of Zr in the matrix. Comparison with a physical mixture of zirconium oxide with silica aerogel shows that the Zr silicate aerogel is significantly more active, and the physical mixture primarily produces carbon dioxide. Next, the effect of the greater surface area of the aerogel was studied. A pure zirconia aerogel was made with a surface area of 170 m^2/g and compared to the pure zirconium oxide (probable surface area of a few m^2/g). The aerogel is more active, making mainly carbon dioxide. We further investigated the effect of surface area via sintering studies, finding that the mesopore structure is essentially removed by treatment at 1100°C, and that the activity of the Zr silicate aerogel is reduced to that of thermal reactions alone. Similar results were obtained for the silica aerogel. Current efforts are focused on a statistically designed set of reaction experiments to map out the behavior of Zr silicate aerogel as a function of metal loading, reactant stoichiometry, flow rate, temperature and dilution. In addition, M-Zr silicate systems, where M includes Al, B, B-Ti, and W, are being investigated.

Gas Hydrates of the Arctic

CONTRACT INFORMATION

Contract Number	DE-AI21-83MC20422
Contractor	U.S. Geological Survey 345 Middlefield Road, MS-999 Menlo Park, California 94025 (415) 354-3009
Contractor Project Manager	Timothy S. Collett
Principal Investigators	Kenneth J. Bird Timothy S. Collett Keith A. Kvenvolden Myung W. Lee
METC Project Manager	Rodney D. Malone
Period of Performance	October 1, 1983 to September 30, 1990

ABSTRACT

Sediments of the Arctic region may contain enormous quantities of natural gas in the form of gas hydrates, which are crystalline substances composed of water and mostly methane. These ice-like substances are generally found in two distinct environments: (1) offshore, in sediment of outer continental margins; and (2) in nearshore to onshore areas associated with the occurrence of permafrost.

The presence of gas hydrates in offshore continental margins have been inferred mainly from the occurrence of anomalous bottom-simulating reflectors (BSRs) on marine seismic records. Within the sediments of the Arctic Ocean region, BSRs have been mapped at subbottom depths ranging from about 100 to about 1,100 meters. Onshore in the Arctic gas hydrates are present in western Siberian platform, the Timan-Pechora province, the eastern Siberian craton, and in the northeastern Sinerian and Kamachatka areas of the Soviet Union. In the North American Arctic, well-log responses attributed to the presence of gas hydrates have been obtained in about a fifth of the wells drilled in the Mackenzie Delta, and in the Arctic Islands over half of the wells are inferred to contain gas hydrates. In northern Alaska gas hydrates have been identified in 34 industry wells using well-log responses calibrated to an interval in a well where gas hydrates were recovered in a core. The combined information from Arctic gas-hydrate studies shows that in permafrost regions, gas hydrates exist at subsurface depths ranging from about 130 to about 2,000 meters.

Clathrates in the Arctic Regions

Michael D. Max
Naval Research Laboratory

ABSTRACT

Clathrates (gas hydrates) are medium to high pressure-stabilized, ice-like compounds stabilized by higher than sea level ambient pressure found in the cold, deep-ocean environment, especially the polar oceans. Natural gas, primarily methane, is held within a water molecule crystal lattice and thermodynamically stabilizes the structure through hydrogen bonding. Clathrate forms in the Clathrate Stability Zone (CSZ), a thermodynamically stable zone that extends downward from the sediment surface to a depth determined by the local heat flow and sedimentation rate conditions. The CSZ is thicker in deeper water where pressure is higher. The lower part of the CSZ can become solid and can act as a gas trap, and the base of the CSZ is the pressure-temperature phase boundary of the gas+water/clathrate reaction. From 180 to 200 volumes of gas can be concentrated in one volume of clathrate. Clathrate formation and trapping of gas as a long-term part of marine basin genesis is a first-order concentration process that can hold immense volumes of gas in marine sediment.

Natural gas clathrates (hydrates) probably occur over broad areas of the Arctic Ocean and northern Nordic Sea. By analogy with identifications elsewhere, shallow gas reservoirs can be expected within 1.5 km of the sediment surface of the north polar ocean basins. Clathrates and trapped gas in thickly sedimented areas in the Arctic and Nordic seas have been identified locally in the west Barents Sea and northern Alaska continental margins. Analysis of sediment thickness, sediment types, sedimentation history, and heat flow suggests that widespread generation of gas has been trapped in, and possibly below impermeable clathrate, over 1.5×10^6 km^2 of the Arctic and Atlantic polar region. Clathrates can be expected to occur in sediments of most of the Canada and Wrangel Basins, and along most of the continental slope and rise sediments. If clathrates prove to be developed over the predicted regions, they could hold over 8×10^6 km^3 of natural gas. Clathrates and related gas deposits may thus comprise major energy resources.

Application of Remote Geologic Analysis to Gas Exploration in Devonian Shale

Michael G. Foley
Pacific Northwest Laboratory
Thomas H. Mroz
Morgantown Energy Technology Center
H. Raymond Pratt
EG&G WASC, Inc.

ABSTRACT

Pacific Northwest Laboratory's (PNL) Remote Geologic Analysis (RGA) system uses a unique, automated, pattern-recognition approach to identify potential fracture zones (of any dip from vertical to less than 40°) by coplanar analysis of their geomorphic expression in digital models of topography. For its first oil- and gas-related field trial, the RGA system was applied to the fracture characterization of the Morgantown Energy Technology Center's Study Area 1 in the Big Sandy Gas Field in southwest West Virginia. This site was selected for a blind test of the technology because of the characterization data available from well drilling, gas production, and seismic surveys for evaluating the RGA results. The Morgantown staff used these data and performed a geologic analysis of the region coincidentally, but separately, from the PNL fracture analysis to ensure that a bias would not be introduced into the interpretations. Structure and isopach maps show significant trends in the faulting and folding of the producing formations that control production volumes, which correlate well with the principal interpreted fracture sets from the RGA results. Three fracture sets for the Big Creek, West Virginia, 1:24,000 quadrangle parallel major geologic structures that are associated with basement faulting (steep dip, NE trend) and thrust faulting (60° dip, NW trend). These structures appear, in combination with anticlinal folding, to enhance gas production. To date, only the most prominent fracture planes from the RGA analyses have been correlated with the large-scale structural features (basement faulting) in the study area. The next step in this field trial will be to determine if lesser planar features from the analyses correlate with the detailed structural geology and regional geomorphology of the rocks exposed at the surface.

The PNL part of this work was supported by the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830.

Appendices

Appendix A: Agenda

Natural Gas Research and Development Contractors Review Meeting November 14-15, 1990

WEDNESDAY, NOVEMBER 14, 1990

7:00 a.m.	Registration/Coffee
8:30 a.m.	Welcome Gary V. Latham, Chief, Unconventional Gas Projects Branch Morgantown Energy Technology Center
8:40 a.m.	Opening Remarks Louis A. Salvador, Associate Director, Office of Technical Management Morgantown Energy Technology Center
8:55 a.m.	Introduction Hugh D. Guthrie, Director, Extraction Projects Management Division Morgantown Energy Technology Center
9:00 a.m.	Keynote Address, *Natural Gas: A Clean and Secure Energy for America* Michael Baly III, President American Gas Association

SESSION 1 – UNCONVENTIONAL RESOURCES WESTERN TIGHT GAS

Chairperson: Karl-Heinz Frohne

9:30 a.m.	1.1	*USGS 1990 Activities With Respect to Tight Gas in the Uinta Basin, Utah and Colorado* Thomas D. Fouch U.S. Geological Survey
9:50 a.m.	1.2	*Systems Analysis of Low Permeability Natural Gas Formations in the Western United States* John R. Duda Morgantown Energy Technology Center

10:10 a.m.	BREAK	
10:30 a.m.	1.3	*Geotechnology for Low Permeability Gas Reservoirs* Norman R. Warpinski Sandia National Laboratory
10:50 a.m.	1.4	*An Evaluation of Co-Planar Lineament Analysis and Some Thoughts on Using Surface Geological Data to Predict Subsurface Geology* Allan C. Smith Morgantown Energy Technology Center
11:10 a.m.	1.5	*Technology Extrapolation of MWX Data Into the Piceance Basin* Edwin H. Price CER Corporation
11:30 a.m.	1.6	*Slant Hole Completion Test, Mesaverde Group, Piceance Basin, Colorado* F. Richard Myal CER Corporation
12:00 p.m.	LUNCHEON PRESENTATION Reflections Dining Room Thomas F. Bechtel, Director Morgantown Energy Technology Center	

SESSION 2 – UNCONVENTIONAL RESOURCES EASTERN TIGHT GAS

Chairperson: Albert B. Yost

1:30 p.m.	2.1	*Hydraulic Fracturing of the Devonian Shale With a Non-Damaging Fluid* Raymond L. Mazza Petroleum Consultants, Inc.
1:50 p.m.	2.2	*Multi-Strata Exploration and Production Study* Linda K. Hawkins, Beckley College T. K. Reeves, BDM Engineering Services Company
2:10 p.m.	2.3	*An MWD System for Air Drilling* Llewellyn A. Rubin Geoscience Electronics, Inc.

2:30 p.m.	2.4	*Results of Horizontal Well Site Evaluations in Fractured Devonian Shale Reservoirs* Thomas H. Mroz Morgantown Energy Technology Center
2:50 p.m.	BREAK	
3:10 p.m.	2.5	*Horizontal Wells in the Devonian Shale* William K. Overbey, Jr. BDM Engineering Services
3:30 p.m.	2.6	*Drilling and Completion of a Horizontal Devonian Shale Well in Martin County, Kentucky* Gregory Koziar Columbia Gas System Service
3:50 p.m.	2.7	*Sterling/DOE/GRI Slant Well: A Directional Drilling Case History* Gery Muncey PrimeEnergy Corporation
4:10 p.m.	2.8	*Eastern Gas Systems Analysis Devonian Shales - Tight Sands* Anthony M. Zammerilli Morgantown Energy Technology Center

POSTER SESSION
5:00 - 7:00 p.m.
Chestnut Ridge A&B

P1 *The Geoscience Center at METC*
Thomas H. Mroz, U.S. Department of Energy
Raymond J. Lopez, EG&G WASC, Inc.
Morgantown Energy Technology Center

P2 *Eastern Gas Analysis - A Systems Approach*
Anthony M. Zammerilli and Abbie W. Layne
Morgantown Energy Technology Center

P3 *Systems Analysis of Natural Gas Resources From Low Permeability Formations*
John R. Duda
Morgantown Energy Technology Center

P4 *Geotechnical Evaluations for Siting Horizontal Wells in Devonian Shale Reservoirs*
Thomas H. Mroz, U.S. Department of Energy
William A. Schuller, EG&G WASC, Inc.
Morgantown Energy Technology Center

P5 *Western Tight Gas Sands Research*
Allan C. Smith, U.S. Department of Energy
Susan E. Pool and Mark H. Thomas, EG&G WASC, Inc.
Morgantown Energy Technology Center

P6 *Deep Source Gas Seismic Survey - Washington State*
Mary Guide and Steven C. Krehbiel
Morgantown Energy Technology Center

P7 *Parametric Studies on Catalytic and Non-Catalytic Partial Oxidation of Methane, Ethane and Ethylene*
Abolghasem Shamsi
Morgantown Energy Technology Center

P8 *Natural Gas Recovery/Utilization SBIR Program*
Harold D. Shoemaker
Morgantown Energy Technology Center

P9 *Gas to Liquids*
Lawrence Livermore National Laboratory

P10 *Gas Hydrates of the Arctic*
Timothy S. Collett
U.S. Geological Survey

P11 *Gas Hydrates*
Michael Max
U.S. Navy

P12 *Deep Source Gas*
U.S. Geological Survey

P13 *Application of Remote Geologic Analysis to Gas Exploration in Devonian Shale*
Michael G. Foley, Pacific Northwest Laboratory
Thomas H. Mroz, U.S. Department of Energy
H. Raymond Pratt, EG&G WASC, Inc.

P14 *Natural Gas Display*
Charles W. Byrer
Morgantown Energy Technology Center

THURSDAY, NOVEMBER 15, 1990

7:00 a.m.	Registration/Coffee	
8:30 a.m.	Opening Remarks Gary V. Latham, Chief, Unconventional Gas Projects Branch Morgantown Energy Technology Center	
8:35 a.m.	Keynote Address Robert H. Gentile, Assistant Secretary for Fossil Energy U.S. Department of Energy	

SESSION 3 – CONVENTIONAL/SPECULATIVE RESOURCES

Chairperson: William J. Gwilliam

9:00 a.m.	3.1	*Secondary Natural Gas Recovery: Targeted Technology Applications for Infield Reserve Growth* Robert J. Finley The University of Texas at Austin
9:20 a.m.	3.2	*Deep Gas Seismic* Keith J. Westhusing Morgantown Energy Technology Center
9:40 a.m.	3.3	*Are Hydrocarbon Source Rocks Buried Beneath Volcanic Flows in the Southern Washington Cascades?* William D. Stanley U.S. Geological Survey
10:00 a.m.	3.4	*Potential for Natural Gas Resources in Deep Sedimentary Basins* Dudley D. Rice U.S. Geological Survey
10:20 a.m.	BREAK	
10:40 a.m.	3.5	*Kinetic Models of Hydrocarbon Generation* Jerry J. Sweeney Lawrence Livermore National Laboratory
11:00 a.m.	3.6	*Terrestrial Gas Hydrate Occurrences* Timothy S. Collett U.S. Geological Survey

11:20 a.m. 3.7 *Study of Hydrate Dissociation by Methanol and Glycol Injection*
Vidyadhar A. Kamath
University of Alaska

11:40 a.m. 3.8 *Seismic Interpretation of Gas Hydrates in the Blake Ridge Area*
William P. Dillon
U.S. Geological Survey

12:00 p.m. LUNCH
Reflections Dining Room

SESSION 4 – GAS TO LIQUIDS

Chairperson: Rodney D. Malone

1:00 p.m. 4.1 *Fuel Cells: A Gas Utilization Technology for the 1990's?, 2000's?*
Rita A. Bajura
Morgantown Energy Technology Center

1:30 p.m. 4.2 *PETC's Natural Gas Conversion Program*
Gary J. Stiegel
Pittsburgh Energy Technology Center

1:50 p.m. 4.3 *Gas Phase and Catalytic Partial Oxidation Reactions of Methane and Oxygen*
Michael W. Droege
Lawrence Livermore National Laboratory

2:10 p.m. 4.4 *Methane Oxidation Over Dual Redox Catalysts*
Kamil Klier
Lehigh University

2:30 p.m. BREAK

2:50 p.m. 4.5 *Methane to Methanol Conversion*
Francis T. Finch
Los Alamos National Laboratories

3:10 p.m. 4.6 *Suprabiotic Catalyst Systems for Selective Oxidation of Light Alkane Gases to Fuel Oxygenates*
James E. Lyons
Sun Refining and Marketing Company

3:30 p.m. 4.7 *Catalytic Assessment of Methane Conversion to Liquid Fuels*
Daniel J. Driscoll
Morgantown Energy Technology Center

Appendix B: METC Participants

Rita A. Bajura, Director
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Jim Burchfield, General Engineer
304/291-4634, Mailstop E06

John W. Byam, Deputy Director
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Joy Cumley, Branch Secretary
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Melodie DeWitt, Budget Analyst
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John Duda, Petroleum Engineer
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John Guide, Project Manager
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John Kovach, Chief
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Joseph W. Lagler, Petroleum Engineer
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David Zalewski, Research Chemist
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Anthony Zammerilli, Petroleum Engineer
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Appendix C: Other Participants

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